

# 3. Oxidation and Corrosion of Alloys

- a. Review of thermodynamic principles
- b. Review of diffusion principles Point Defects in Metals and Oxides
- c. Oxide stoichiometry and defect chemistry
  - Anionic and cationic diffusion
  - Defect chemistry modification
  - Stoichiometry and growth
  - Stoichiometry and electrical conduction

# Oxidation and Corrosion of Alloys (continued)

## d. Principles of oxidation and corrosion

- Parabolic and transition from parabolic
- External vs. internal oxidation (Selective oxidation)
- Oxide adherence
- Environmental influences in hydrogen fueled SOFCs (Evaporation, H<sub>2</sub>O content, dual-atmosphere, pressure, current density, breakaway corrosion...)
- Corrosion mechanisms using complex fuels (Oxidation in multi component gases, Carburization, sulfidation, deposit effects)
- Interaction between adjacent SOFC components

# Thermodynamic Principles

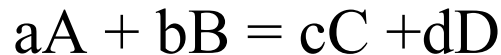
$$G' = H' - TS'$$

At constant temperature and pressure:

$\Delta G' < 0$  spontaneous reaction expected

$\Delta G' = 0$  equilibrium

$\Delta G' > 0$  thermodynamically impossible process



$$\Delta G' = \Delta G^\circ + RT \ln \left( \frac{a_C^c a_D^d}{a_A^a a_B^b} \right)$$

$$a_i = \frac{p_i}{p_i^\circ}$$

$$\Delta G^\circ = c\Delta G_C^\circ + d\Delta G_D^\circ - a\Delta G_A^\circ - b\Delta G_B^\circ$$

At equilibrium:

$$\Delta G^\circ = -RT \ln \left( \frac{a_C^c a_D^d}{a_A^a a_B^b} \right)_{eq} = -RT \ln K$$

Note: Free energy of formation data can be accessed either directly or as “Log K<sub>p</sub>”. The latter allows direct calculation of the equilibrium constant for the overall reaction.

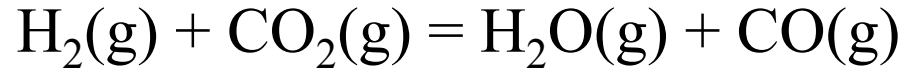


# Calculation of Activities in a Gaseous Environment

**Problem** A gas consisting of 60 vol %  $H_2$  and 40 vol%  $CO_2$  is let into a reaction chamber and heated to 1200K at a total pressure of 1 atm. Calculate the oxygen partial pressure and carbon activity in this gas when it comes to equilibrium.

**Solution** The common species which can form in such a gas mixture and their  $\log K_p$  values at 1200K are listed in the following table.

<u>Species</u>	<u><math>\log K_p</math></u>
$CO_2$	17.243
$CO$	9.479
$H_2O$	7.899
$H_2$	0.00



$$\log K_R = \log K_P^{H_2O} + \log K_P^{CO} - \log K_P^{CO_2} = 0.135$$

$$K_R = 1.365 = \frac{p_{H_2O} p_{CO}}{p_{H_2} p_{CO_2}}$$

$$p_i = \frac{n_i}{n_{tot}} P_{tot}$$

$$K_R = 1.365 = \frac{n_{H_2O} n_{CO}}{n_{H_2} n_{CO_2}}$$

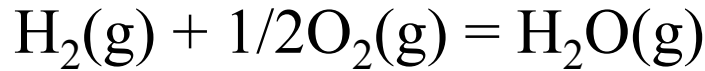
<u>Species</u>	<u>Initial Comp. (moles)</u>	<u>Final Comp. (moles)</u>
H <sub>2</sub>	0.6	0.6- $\lambda$
CO <sub>2</sub>	0.4	0.4- $\lambda$
CO	0	$\lambda$
H <sub>2</sub> O	0	$\lambda$

$$K_R = 1.365 = \frac{\lambda\lambda}{(0.6 - \lambda)(0.4 - \lambda)} \quad \lambda = 0.2575 \text{ moles.}$$

<u>Species</u>	<u>Final Comp. (moles)</u>	<u>Partial Pressures (atm)</u>
H <sub>2</sub>	0.3425	0.3425
CO <sub>2</sub>	0.1425	0.1425
CO	0.2575	0.2575
H <sub>2</sub> O	0.2575	0.2575

## Calculation of Activities

### Oxygen Partial Pressure



$$K_P = 7.924 \times 10^7 = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{O}} p_{\text{O}_2}^{1/2}} = \frac{0.2575}{0.3425 p_{\text{O}_2}^{1/2}}$$

$$p_{\text{O}_2} = 9.0 \times 10^{-18} \text{ atm}$$

### Carbon Activity

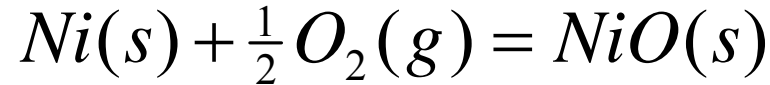


$$\log K_R = \log K_P^{\text{CO}_2} - 2 \log K_P^{\text{CO}} = -1.715$$

$$K_R = 0.193 = \frac{p_{\text{CO}_2} a_{\text{C}}}{p_{\text{CO}}^2} = \frac{0.1425 a_{\text{C}}}{(0.2575)^2}$$

$$a_{\text{C}} = 0.009$$

Will this gas oxidize Ni or Cr?

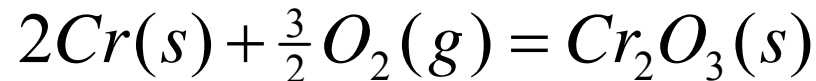


$$\text{Log } K_p = 5.75$$

$$K_p = \frac{1}{p_{O_2}^{\frac{1}{2}}} = 5.6 \times 10^5$$

$$p_{O_2}^{eq} = 3.2 \times 10^{-12} \text{ atm}$$

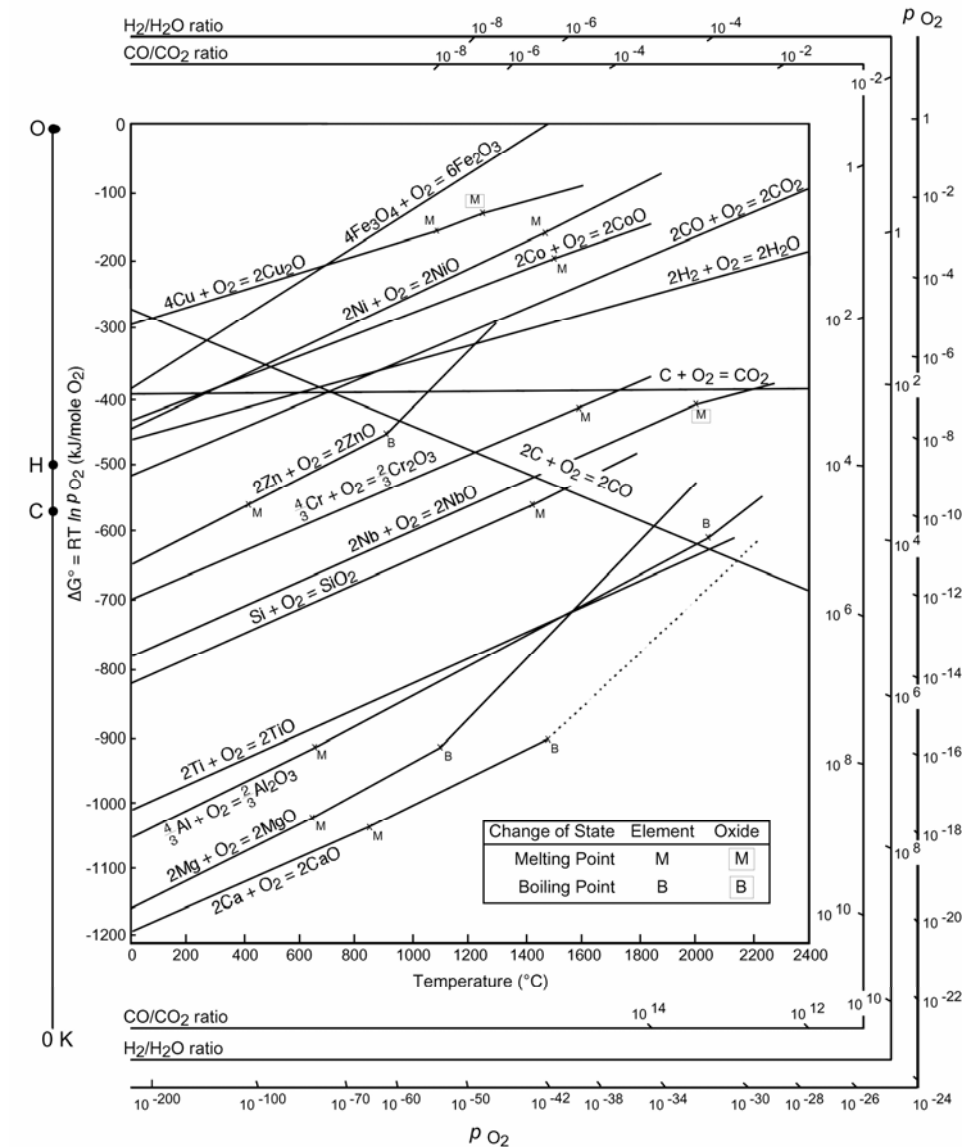
**Ni cannot oxidize**



$$p_{O_2}^{eq} = 1.2 \times 10^{-24} \text{ atm}$$

**Cr will tend to oxidize**

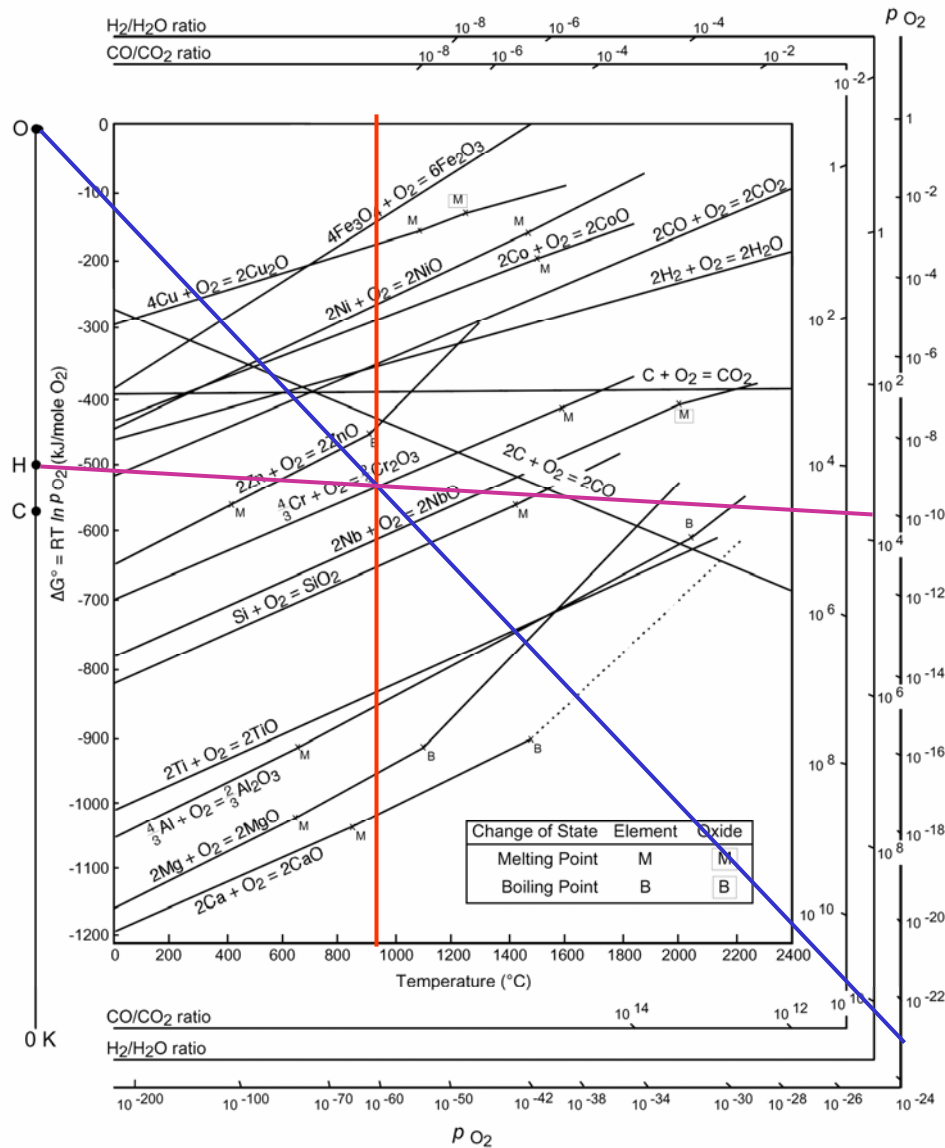
# Ellingham Diagram



# Ellingham Diagram

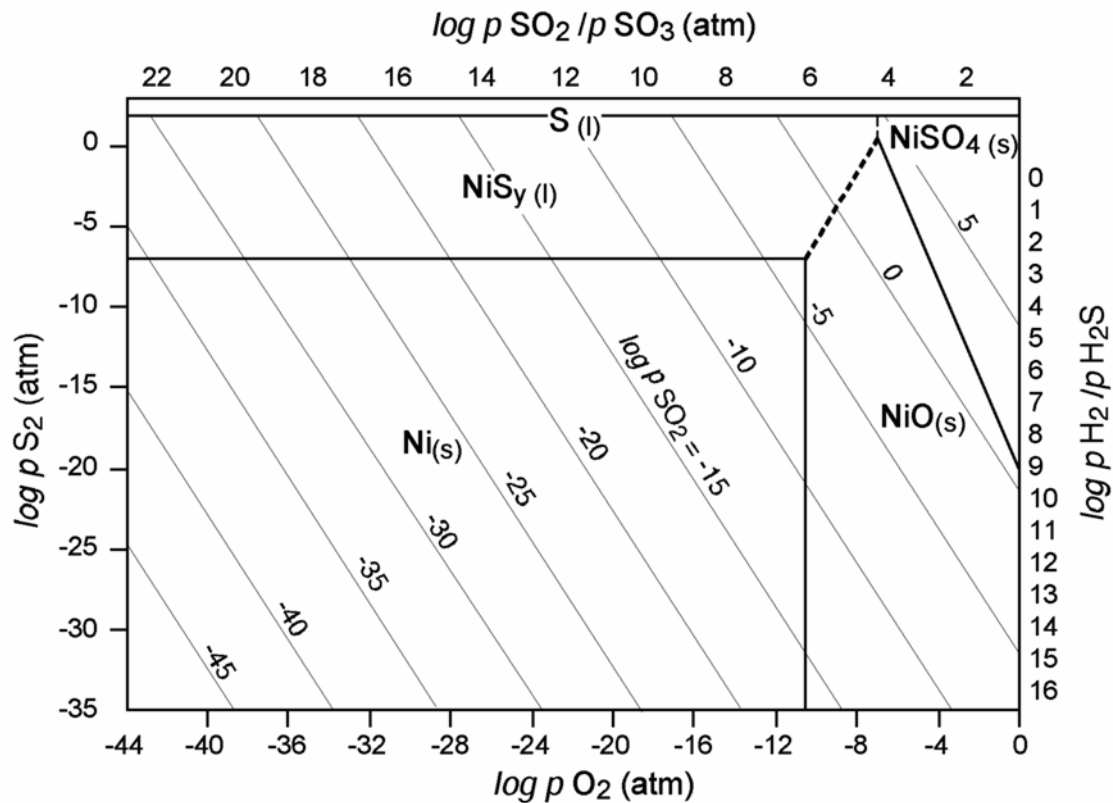
$$p_{O_2} = 9.0 \times 10^{-18} \text{ atm}$$

$$\frac{p_{H_2}}{p_{H_2O}} = 1.33$$



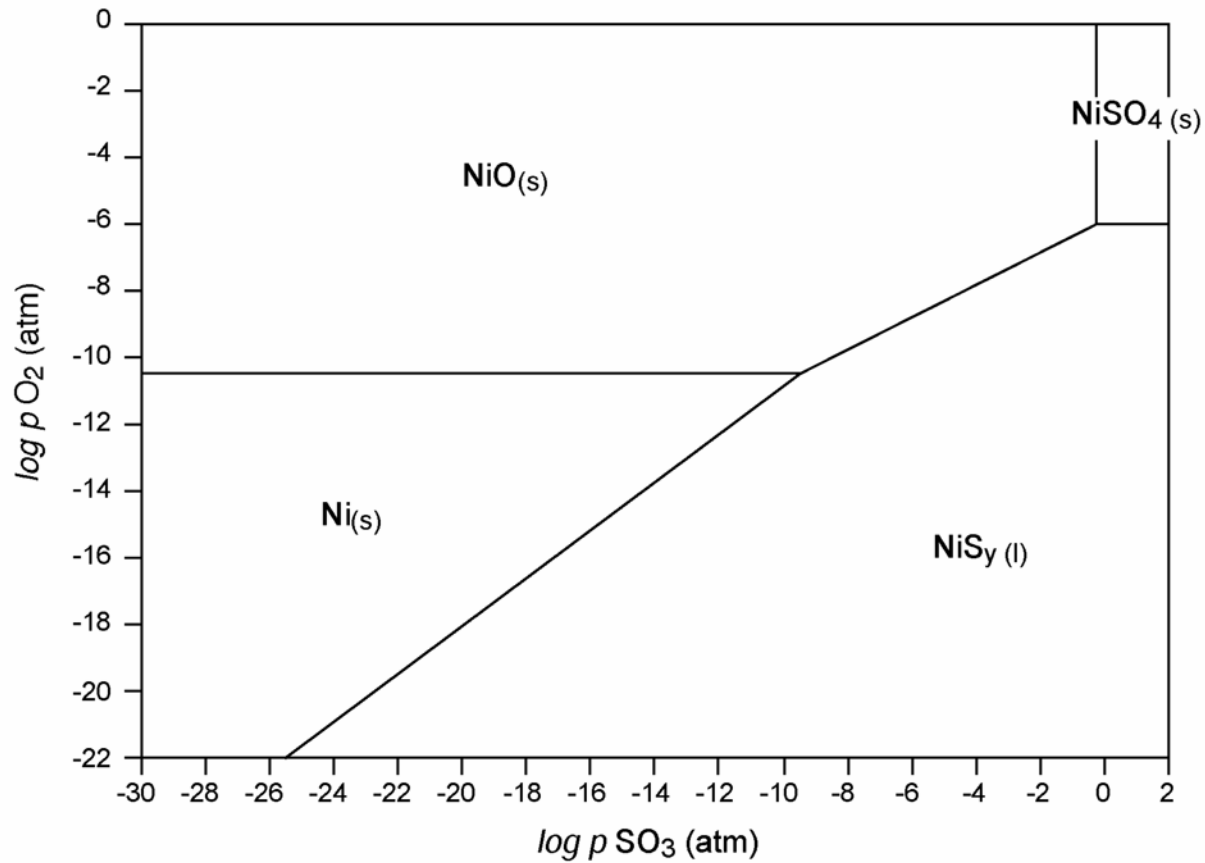
# Isothermal Stability Diagram

## Ni-S-O System, 1250K

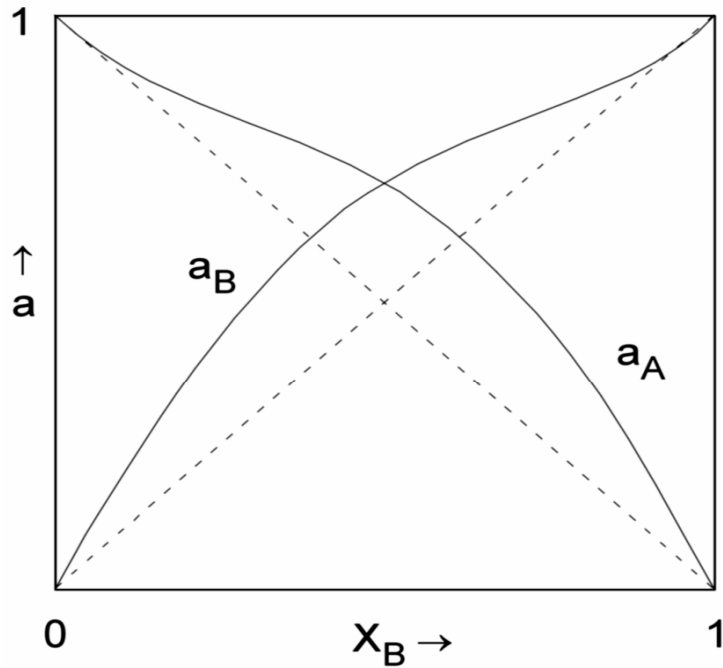




# Isothermal Stability Diagram Ni-S-O System, 1250K

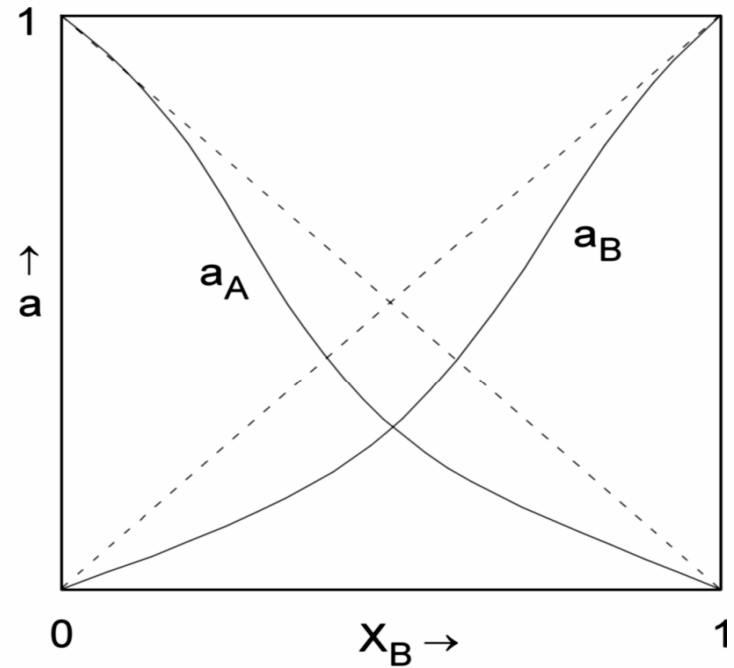


# Solution Thermodynamics



(a)

**Positive Deviation  
from Ideality**



(b)

**Negative Deviation  
from Ideality**

# Solution Thermodynamics

$a_i = N_i$	Ideal Solution
$a_i = \gamma_i N_i$	Real Solution, $\gamma_i = f(N_i)$
$a_i = \gamma_i(\infty) N_i$	Dilute Solution, $\gamma_i(\infty) = \text{constant}$

## Sievert's Law

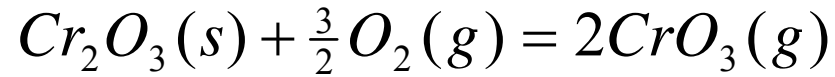
Consider Hydrogen Dissolving into Nickel

$$\frac{1}{2} H_2(g) = \underline{H(inNi)}$$

$$K = \frac{a_H}{p_{H_2}^{1/2}} = \frac{\gamma_H(\infty) N_H}{p_{H_2}^{1/2}}$$

$$N_H = \frac{K}{\gamma_H(\infty)} p_{H_2}^{1/2} = k_S p_{H_2}^{1/2}$$

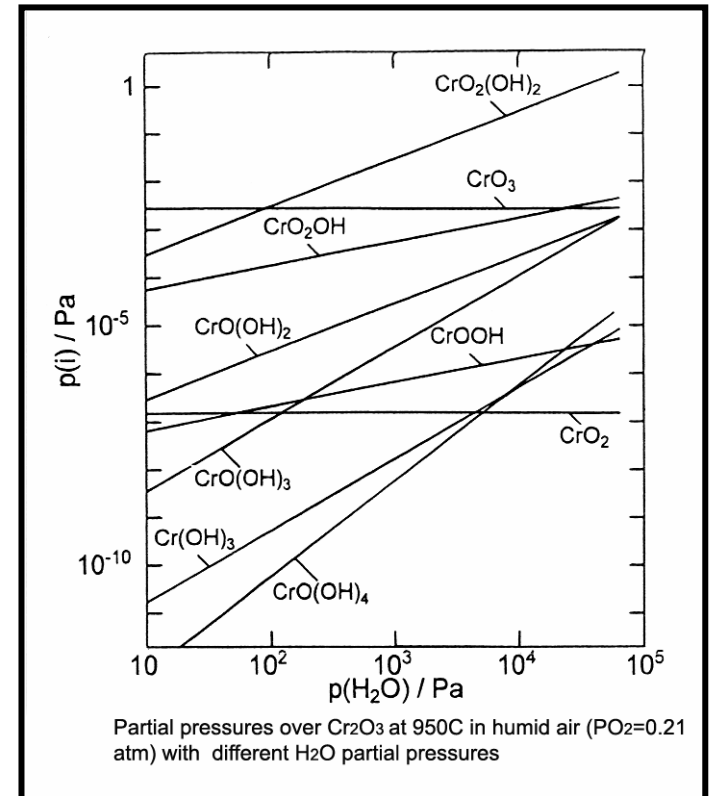
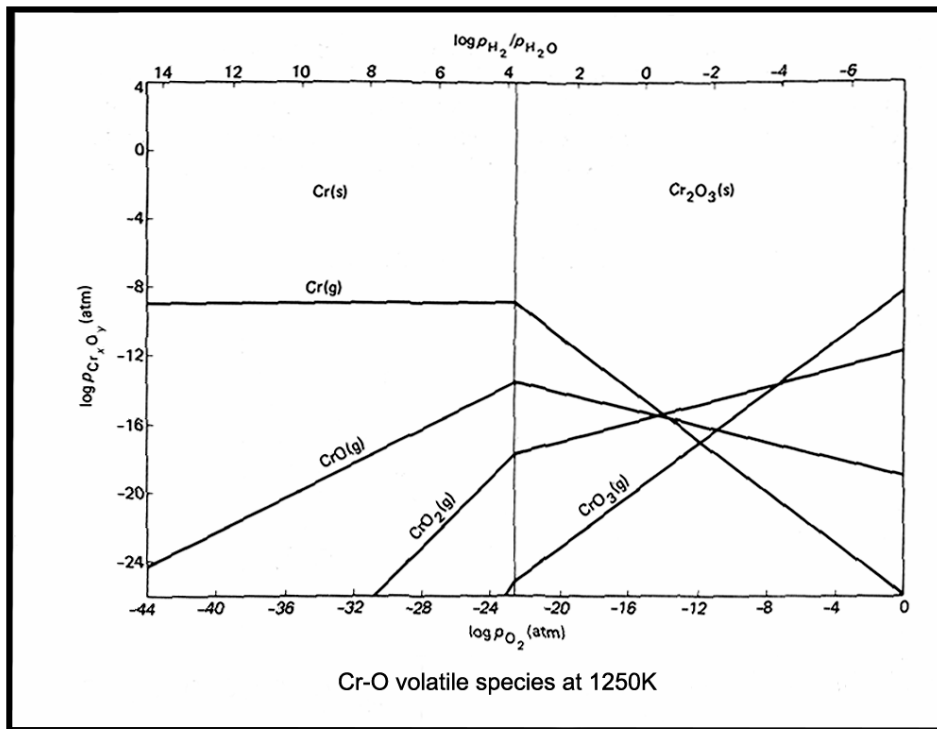
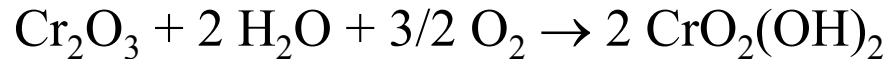
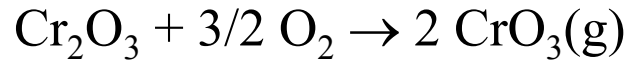
# Chromia Evaporation



$$p_{\text{CrO}_3} = K^{\frac{1}{2}} a_{\text{Cr}_2\text{O}_3}^{\frac{1}{2}} p_{\text{O}_2}^{\frac{3}{4}}$$

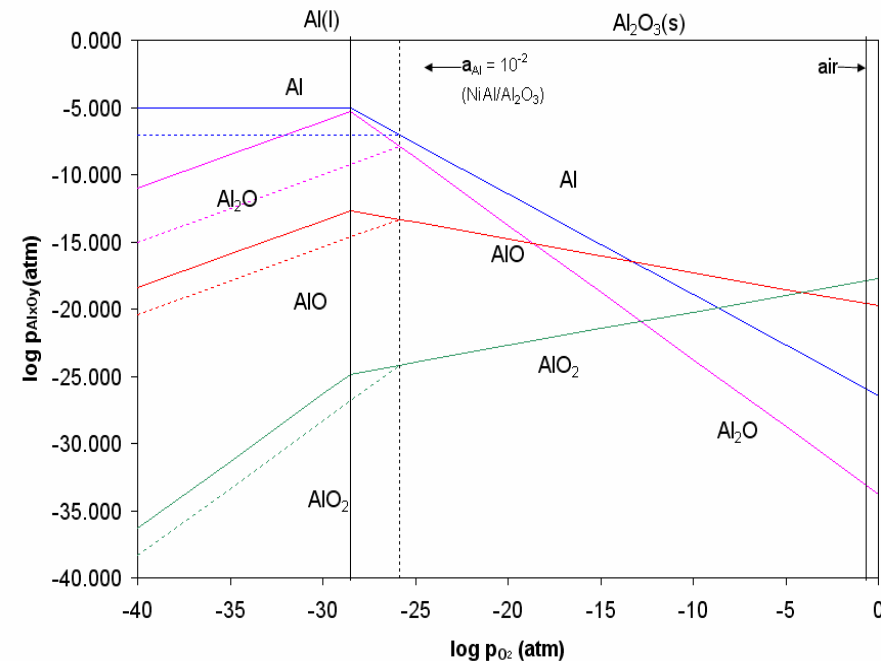
# CHROMIA

- At high T and high  $PO_2$  volatile oxides develop

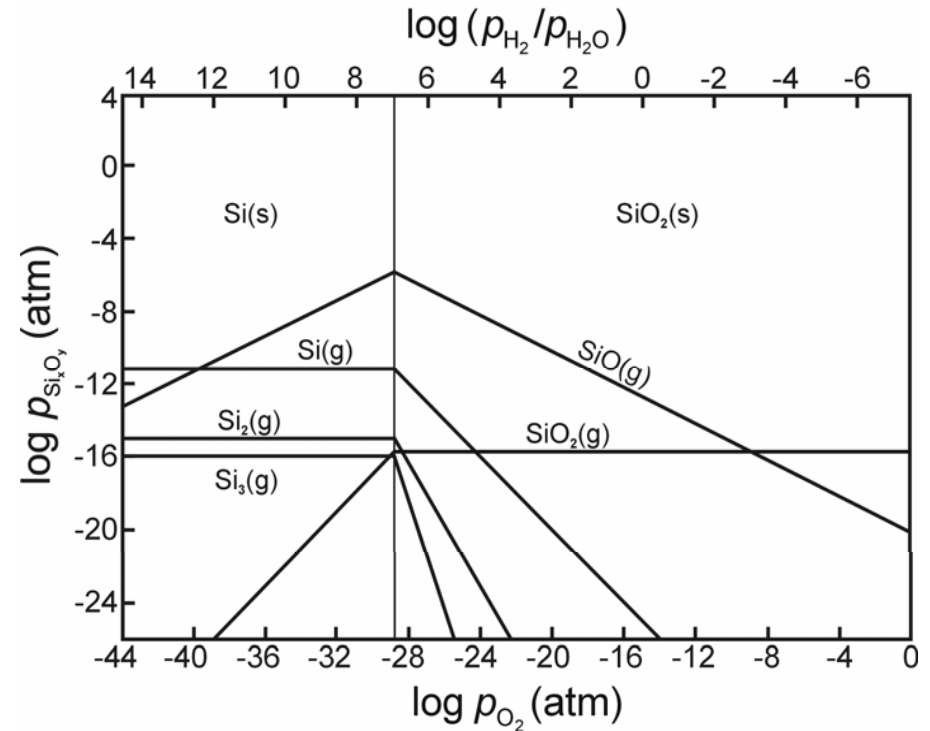


# Vapor Species Diagrams for the Al-O and Si-O Systems

Al – O 1473K



Si – O 1250K



# Diffusion Fundamentals

$$J_B = -\tilde{D} \frac{\partial C_B}{\partial x}$$

**Fick's First law**

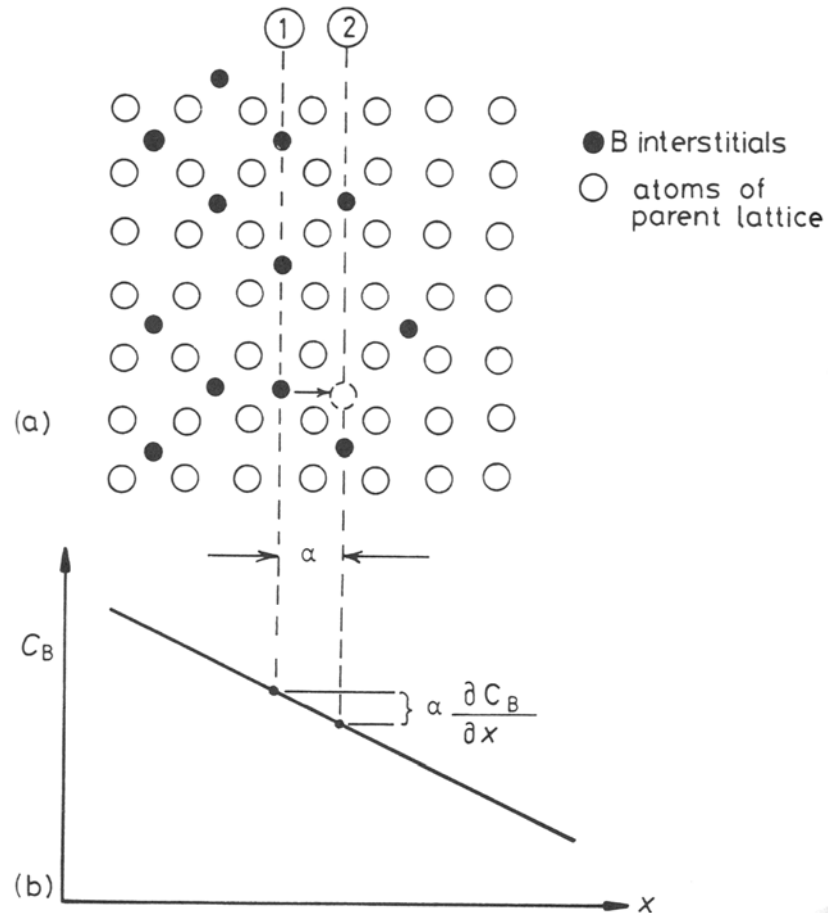
$$\frac{\partial C_B}{\partial t} = \tilde{D} \frac{\partial^2 C_B}{\partial x^2}$$

**Fick's Second Law**

# Diffusion of Interstitial Atoms (e.g. H, C) in a Metal

$$J_B = -\tilde{D} \frac{\partial C_B}{\partial x}$$

$$\frac{\partial C_B}{\partial t} = \tilde{D} \frac{\partial^2 C_B}{\partial x^2}$$



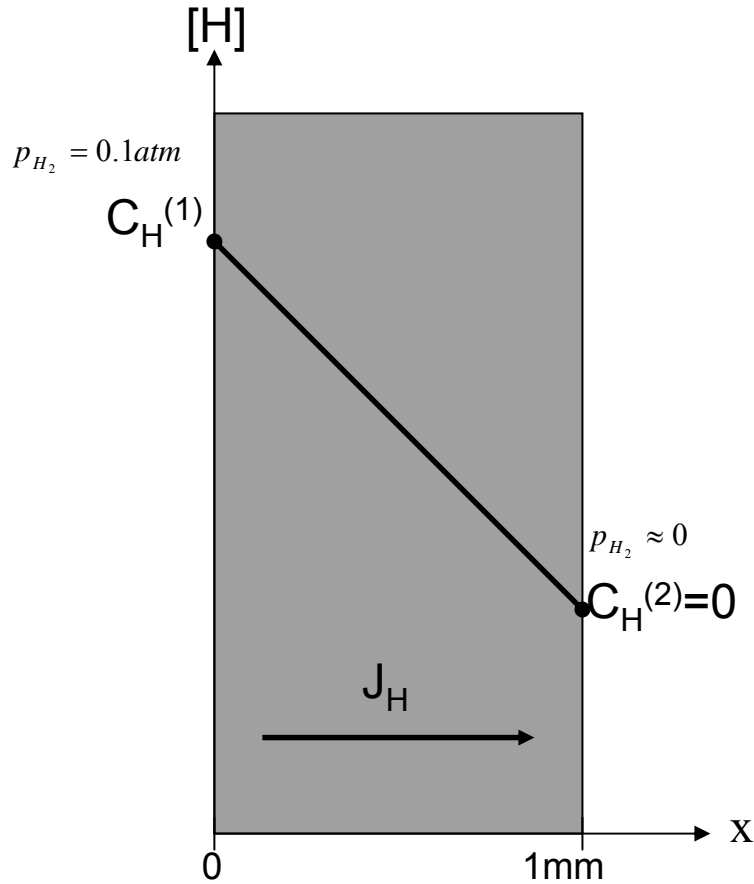


# Fick's First Law

**Steady-State Flux of Hydrogen Through Nickel**

# Steady State Diffusion of H<sub>2</sub> Through Ni

## T=800°C

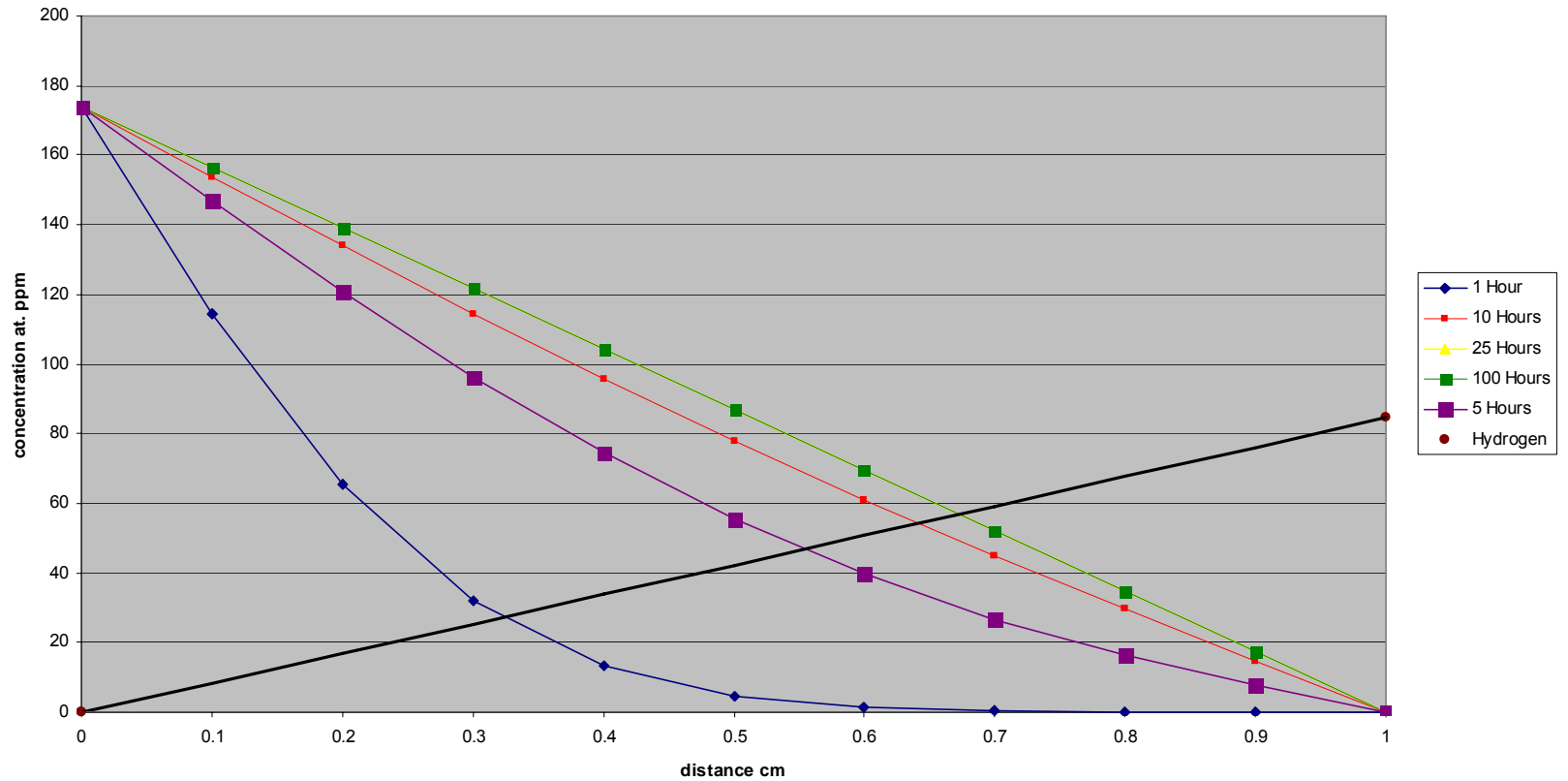


$$J_H = -D_H \frac{dc}{dx} = -D_H \frac{C_H^2 - C_H^1}{x}$$

$$J_H = D_H \frac{C_H^1}{x} = 6.88 \times 10^{-5} (\text{cm}^2 / \text{s}) \frac{2.09 \times 10^{-5} (\text{g} / \text{cm}^3)}{0.1 (\text{cm})}$$

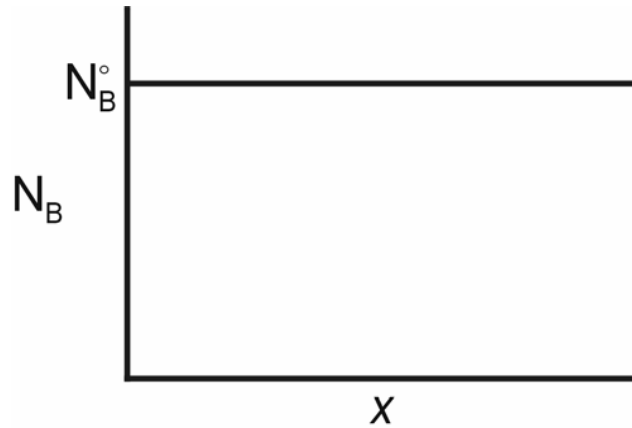
$$J_H = 1.44 \times 10^{-8} (\text{g} / \text{cm}^2 \cdot \text{s})$$

# Oxygen and Hydrogen Concentration Profiles in Nickel

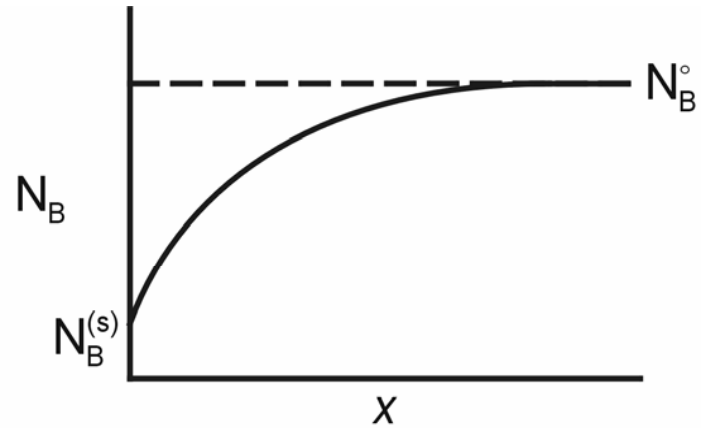


# Fick's Second Law

## Concentration Profile for a Solute B Being Lost by Evaporation



a.



b.

$$\frac{\partial N_B}{\partial t} = \tilde{D} \frac{\partial^2 N_B}{\partial x^2}$$

Boundary Conditions: At time  $t$ :  $N_B = N_B^{(s)}$  at  $x = 0$

$$N_B = N_B^0 \quad \text{at } x = \infty$$

$$Z = \frac{x}{2\sqrt{\tilde{D}t}}$$

$$\frac{-x}{\sqrt{\tilde{D}t^3}} \frac{dN_B}{dZ} = \frac{1}{t} \frac{d^2 N_B}{dZ^2}$$

$$y \equiv \frac{dN_B}{dZ}$$

$$y = -\frac{\sqrt{\tilde{D}t}}{x} \frac{d^2 N_B}{dZ^2} = -\frac{1}{2Z} \frac{d^2 N_B}{dZ^2}$$

$$y = -\frac{1}{2Z} \frac{dy}{dZ}$$

$$-2ZdZ = \frac{dy}{y}$$

$$-Z^2 = \ln y - \ln A$$

$$\frac{dN_B}{dZ} = A \exp(-Z^2)$$

**Boundary Conditions:**

At time t:  $N_B = N_B^{(S)}$  at  $Z=0$   
 $N_B = N_B^o$  at  $Z=\infty$

$$\int_{N_B^{(S)}}^{N_B^o} dN_B = A \int_0^\infty \exp(-Z^2) dZ$$

$$\text{R.H. Integral} = \frac{\sqrt{\pi}}{2}$$

$$A = \frac{2}{\sqrt{\pi}} \left( N_B^o - N_B^{(S)} \right)$$

$$\int_{N_B^o}^{N_B} dN_B = \frac{2(N_B^o - N_B^{(S)})}{\sqrt{\pi}} \int_{\infty}^Z \exp(-Z^2) dZ$$

$$N_B - N_B^o = -\frac{2(N_B^o - N_B^{(S)})}{\sqrt{\pi}} \int_Z^{\infty} \exp(-Z^2) dZ = -(N_B^o - N_B^{(S)}) \operatorname{erfc}(Z)$$

$$\frac{N_B - N_B^o}{N_B^{(S)} - N_B^o} = \operatorname{erfc}(Z)$$

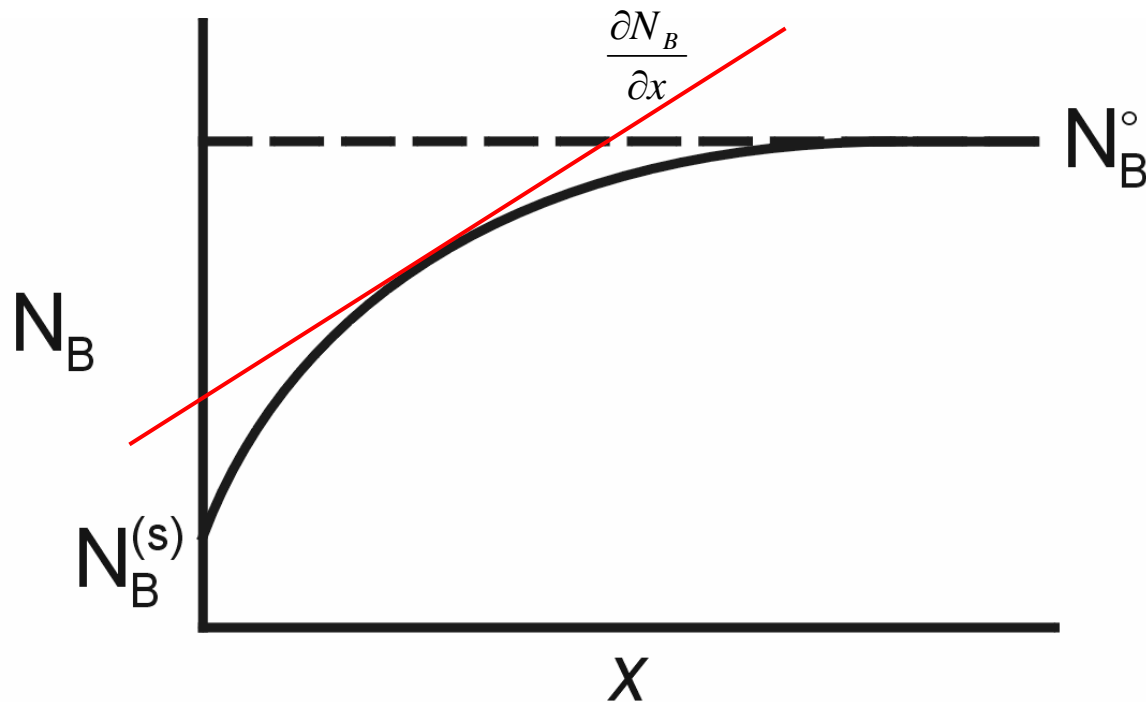
$$\frac{N_B - N_B^{(S)}}{N_B^o - N_B^{(S)}} = \operatorname{erf}(Z)$$

$$N_B = N_B^{(S)} + (N_B^o - N_B^{(S)}) \operatorname{erf}\left(\frac{x}{2\sqrt{\tilde{D}t}}\right)$$

**General Solution**

$$N_B = A_1 + B_1 \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

# Calculation of Local Flux



$$J_B = -\tilde{D} \frac{\partial C_B}{\partial x} = -\tilde{D} V_m \frac{\partial N_B}{\partial x}$$



# Oxide Chemistry

## Point Defects in Metals

- Point defects are thermodynamically stable because they lower the free energy of the system by significantly affecting the entropy of the system. The important point defects in the metals are:

Vacancies  
Interstitials  
Divancies  
Foreign atoms  
Associated complexes of the above

- The equilibrium concentration of the defects is obtained by minimizing the free energy and is given by,

$$C_d = \frac{n}{N} = \exp\left(-\frac{\Delta H_{Form}^d}{kT}\right) \exp\left(\frac{\Delta S_{Form}^d}{k}\right)$$

where;

$C_d$  = concentration of defects

$n$  = number of defects

$N$  = number of lattice sites

$\Delta H_{Form}^d$  = Enthalpy or energy to form defects

$\Delta S_{Form}^d$  = Entropy of formation of defects

- Estimation of  $\Delta S_{Form}^d$  is obtained by considering vibrational entropy of crystal and treating atoms as harmonic oscillators.

## Defect Motion in Metals:

$$w_d \left( \frac{\text{jumps}}{\text{sec}} \right) = v e^{\frac{\Delta S_m^d}{k}} e^{\frac{-\Delta H_m^d}{kT}}$$

$$D_d = \frac{\alpha^2}{6} v e^{\frac{\Delta S_m^d}{k}} e^{\frac{-\Delta H_m^d}{kT}}$$

$$w_{atom} = C_d Z w_d$$

$$D_{atom} = \frac{\alpha^2}{6} w_{atom} = \frac{\alpha^2}{6} C_d Z w_d$$

$$D_{atom} = \frac{\alpha^2}{6} Z v e^{\frac{(\Delta S_F^d + \Delta S_m^d)}{k}} e^{\frac{-(\Delta H_F^d + \Delta H_m^d)}{kT}}$$

$D_{atom}$  is an ideal diffusion coefficient or tracer diffusion coefficient. In an alloy AB where  $\gamma_a$  is the activity coefficient of A,  $C_A$  the concentration of A, and  $N_A$  and  $N_B$  are mole fractions.

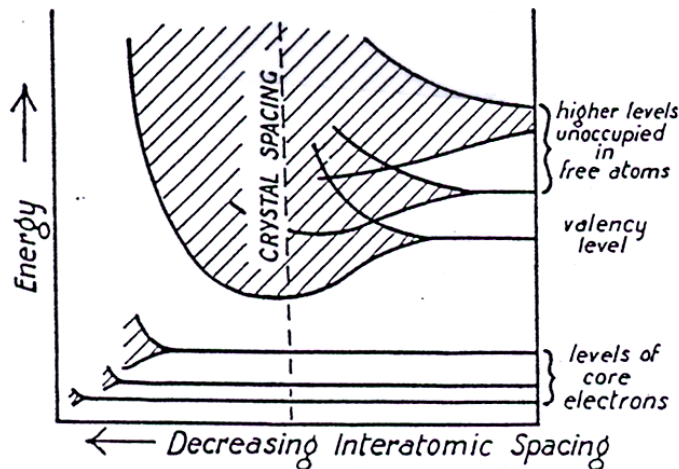
Intrinsic diffusion coefficient: 
$$D_A = D_{atomA}^{ideal} \left( 1 + \frac{\delta \ln \gamma_A}{\delta \ln C_A} \right)$$

Interdiffusion coefficient: 
$$\tilde{D} = N_B D_A + N_A D_B$$

# Point Defects on Elemental Semiconductors

The important point defects in elemental semiconductors are:

- Vacancies
- Interstitials
- Foreign atoms
- Electrons
- Holes
- Charge defects involving the above
- Various associated complexes of the above

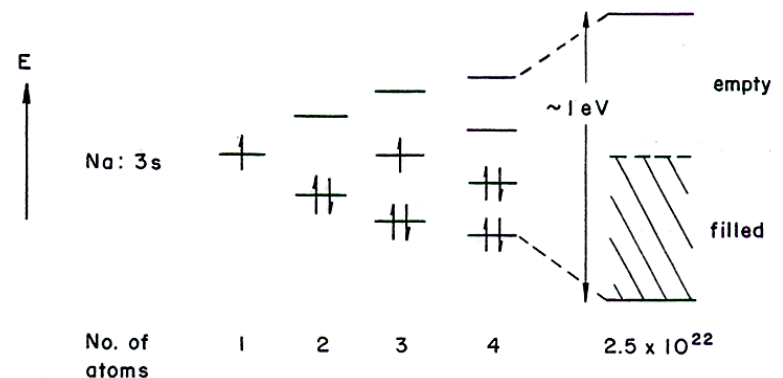


Broadening of atomic energy levels when atoms approach to form a crystal

## Important Electron Theory Concepts

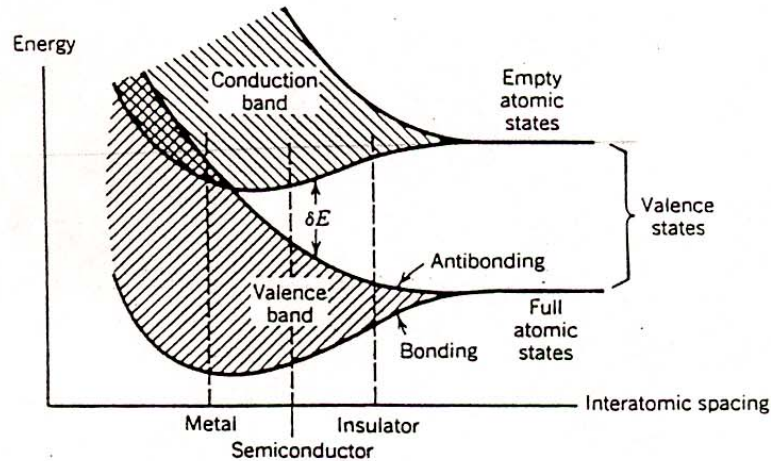
### Concepts of Discrete Energy States

Schematic energy diagram showing the energy of all the atoms in a condensed material at various interatomic spacings. At large atomic spacings the energy levels are discrete, but as the atoms come closer together there is interaction between the atoms which result in splitting of energy levels. The total number of electronic states in a system derives directly from the electronic states of the component atoms and must be conserved.

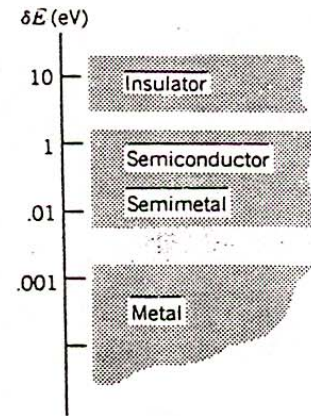


Development of an energy band from the 3s electrons of sodium.

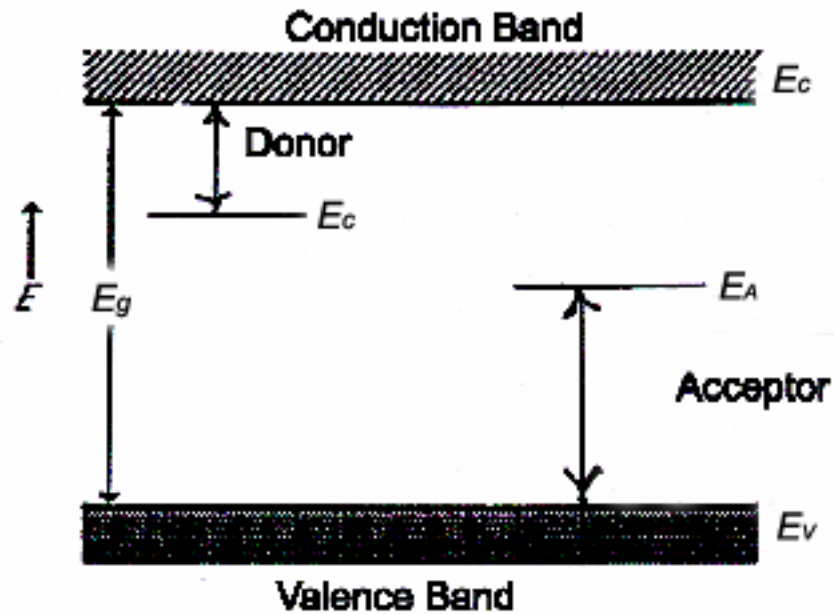
Depending on the atomic spacing and the configuration of the bands, we can have a metal, semiconductor or an insulator.



Electronic energies for a solid as a function of interatomic spacing. At large spacings, all solids show an atomic limit and at small spacings all show a metallic limit (see the text for some qualifications).



The energy needed to raise a solid to electronically excited state, showing ranges of val. corresponding to metals, semiconductors, and insulators at normal temperatures.



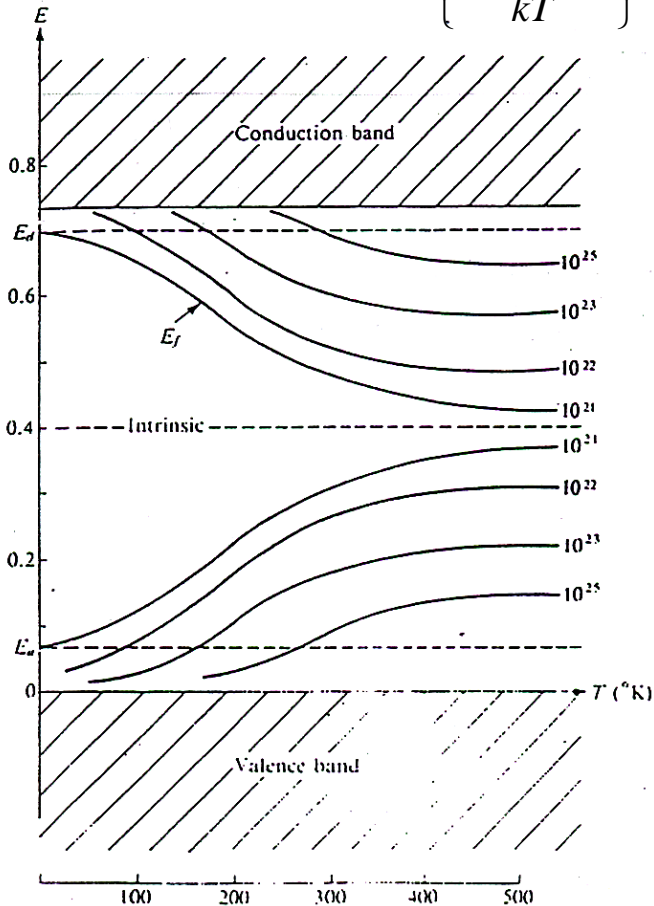
- Intrinsic and Extrinsic Elemental Semiconductors

$$\text{Intrinsic: } n = p = K_i^\circ e^{-\frac{E_g}{2bT}}$$

$$\text{Extrinsic: } np = K_i^\circ e^{-\frac{E_g}{bT}}$$

-ionized native defects and dopants

Electrons	Acceptors	Electron Holes	Donors
$N_c \exp \left\{ \frac{E_F - E_C}{kT} \right\} + \frac{N_A}{\exp \left\{ \frac{E_A - E_F}{kT} \right\} + 1} = N_v \exp \left\{ \frac{E_V - E_F}{kT} \right\} + \frac{N_D}{\exp \left\{ \frac{E_F - E_D}{kT} \right\} + 1}$			



As shown, the Fermi level is a function of the donor or acceptor levels for completely ionized defects

Fermi level as a function of charge carrier concentration per cm<sup>3</sup> and temperature

# Defects on Compounds (Oxides)

## Defect Notations

- **The main symbol:** The defect species, which may be an ion, indicated by the atomic symbol for the species, or a vacant lattice site, denoted by V.
- **The subscript:** Indicates the lattice or interstitial site, I, occupied by the defect.
- **The superscript:** Indicates the difference in charge at the defect site relative to the charge at that site in the perfect crystal. A dot is used for an extra positive charge, and a slash denotes an extra negative charge.

### Examples of Kröger–Vink defect notation

	What <sup>charge</sup> where
Cation vacancy in NaCl	$V_{Na}^{\cdot\cdot}$
Cation interstitial in AgBr	$Ag_I^{\cdot}$
Anion vacancy in MgO	$V_O^{\cdot\cdot}$
Cation interstitial in $Al_2O_3$	$Al_I^{\cdot\cdot\cdot}$
$Ca^{2+}$ substituted for $Na^+$ in NaCl	$Ca_{Na}^{\cdot}$
$Mg^{2+}$ substituted for $Ti^{4+}$ in $TiO_2$	$Mg_{Ti}^{//}$
$O^{2-}$ substituted for $F^-$ in $CaF_2$	$O_F^{\cdot}$

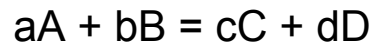
### Important Defects:

Vacancies (cations and anions)  
 Interstitials  
 Foreign atoms  
 Electrons and holes  
 Charged defects  
 Various associated complexes

# Conservation Rules

- **Conservation of mass:** Atoms are neither created nor destroyed within a system, but must be conserved
- **Conservation of charge:** The bulk of an ideal crystal is electrically neutral. Charged defects must be created in combinations that are electrically neutral. Matter can be added to or removed from a crystal only in electrically neutral combinations.
- **Conservation of structure** (lattice site ratios): The creation of lattice defects must not violate the inherent ratio of cation sites to anion sites in the structure. Thus cation and anion sites can be created or destroyed only in ratios that correspond to the stoichiometry of the compound (i.e., in electrically neutral combinations).
- **Conservation of electronic states:** The total number of electronic sites in a system derives directly from the electronic states of the component atoms, and must be conserved.

Law of Mass Action is Applicable



$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = e^{-\frac{\Delta G^\circ}{bT}}$$

Replace activities with concentrations



# Stoichiometry and Defect Chemistry

- Intrinsic Ionic Disorder is such that the stoichiometry of the compound is maintained.

**Example:** Schottky Disorder for the compound  $M_mX_n$ .

$$\frac{[V_M^x]}{[V_X^x]} = \frac{m}{n}$$

$$[V_M^x]^m [V_X^x]^n = K_s$$

- These defects can be ionized

$$V_M^x = V_M^{n-} + nh^\bullet$$

$$V_X^x = V_X^{m\bullet} + me'$$

$$[V_M^{n-}]^m [V_X^{m-}]^n = K'_s$$

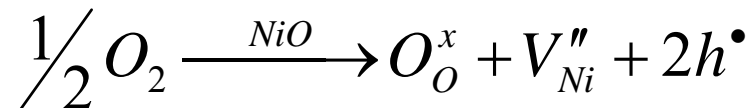
- There are nine types of intrinsic disorder.

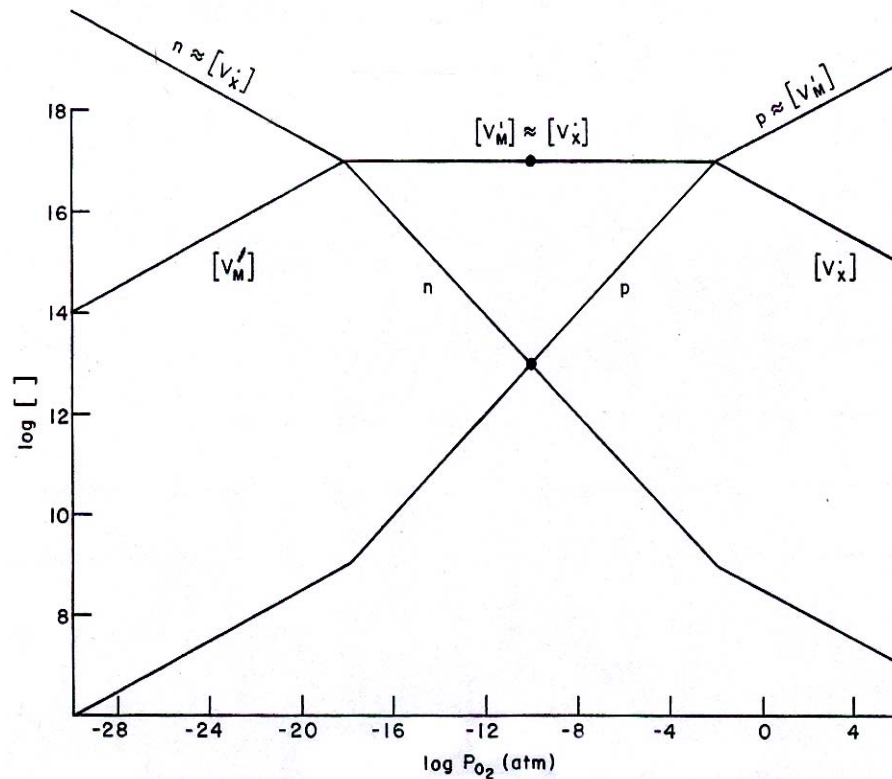
- Extrinsic Ionic Disorder usually involves the addition of a dopant, but there are also cases where such disorder can be established by reactions of the compound with the gas and stoichiometry is not maintained.

**Dopant:**



**Gas Reaction:**





The Kröger-Vink diagram for MX.

Pure MX

No Dopant - Schottky Defects

Electrical Neutrality

$$n + [V'_M] = p + [V^\bullet_X]$$

Constant Temperature

- whether electronic or ionic conductor depends upon:

$$[V'_M][V^\bullet_X] = K_s$$

$$np = K_i$$

# Construction of Kröger-Vink Diagram

## Region I:

$$\text{If } K_s \gg K_i$$

$$\text{Electrical Neutrality: } [V'_M] = [V_X^\bullet] = K_s^{1/2}$$

$$1. \quad \frac{1}{2} X_2(g) = X_X^x + V_M^x$$

$$K_1 = \frac{[V_M^x]}{P_{X_2}^{1/2}}$$

$$2. \quad V_M^x = V'_M + h^\bullet$$

$$K_2 = \frac{[V'_M]p}{[V_M^x]} = \frac{[V'_M]p}{K_1 P_{X_2}^{1/2}}$$

$$p = \frac{K_2 K_1 P_{X_2}^{1/2}}{K_s^{1/2}}$$

$$3. \quad X_X^x = V_X^x + \frac{1}{2} X_{2(gas)}$$

$$K_3 = [V_X^x] P_{X_2}^{1/2}$$

$$4. \quad V_X^x = V_X^\bullet + e'$$

$$K_4 = \frac{[V_X^\bullet]n}{V_X^x} = \frac{[V_X^\bullet]n P_{X_2}^{1/2}}{K_3}$$

$$n = \frac{K_3 K_4 P_{X_2}^{-1/2}}{K_s^{1/2}}$$

**Region II:**

Electrical Neutrality:  $p = [V'_M]$

$$2. \quad K_2 = \frac{[V'_M]p}{K_1 P_{X_2}^{1/2}}$$

$$p = [V'_M] = (K_1 K_2)^{1/2} P_{X_2}^{1/4}$$

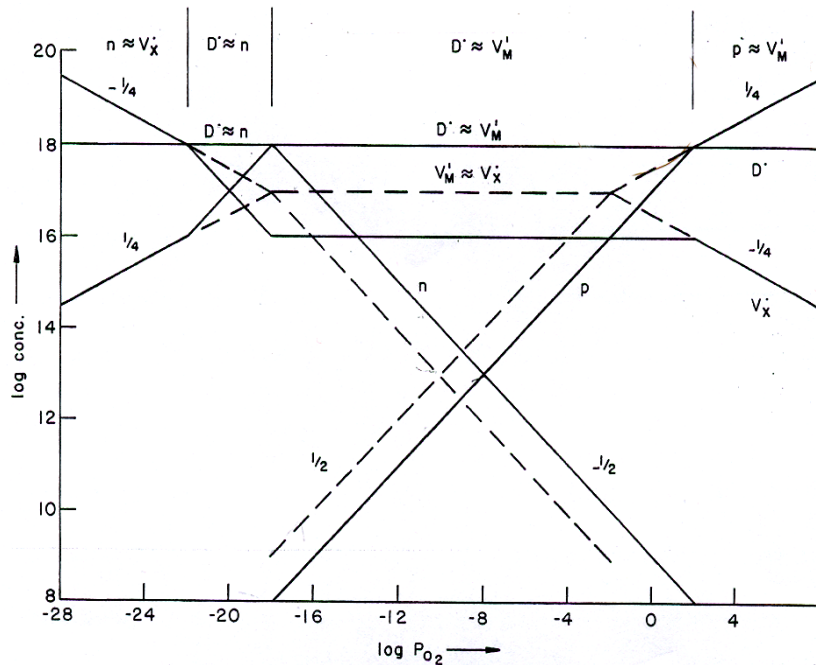
$$[V_x^\bullet] = \frac{K_s}{[V'_M]} = \frac{K_s}{(K_1 K_2)^{1/2}} P_{X_2}^{-1/4}$$

$$n = \frac{K_i}{p} = \frac{K_i}{(K_1 K_2)^{1/2}} P_{X_2}^{-1/4}$$

**Region III:**

Electrical Neutrality:  $n = [V_X^\bullet]$

$$\begin{aligned} 4. \quad K_4 &= \frac{[V_X^\bullet]n}{K_3} P_{X_2}^{1/2} \\ n = [V_X^\bullet] &= (K_4 K_3)^{1/2} P_{X_2}^{-1/4} \\ [V'_M] &= \frac{K_s}{[V_X^\bullet]} = \frac{K_s}{(K_4 K_3)^{1/2}} P_{X_2}^{1/4} \\ p &= \frac{K_i}{n} = \frac{K_i}{(K_4 K_3)^{1/2}} P_{X_2}^{1/4} \end{aligned}$$



Constant Temperature

D is a dopant

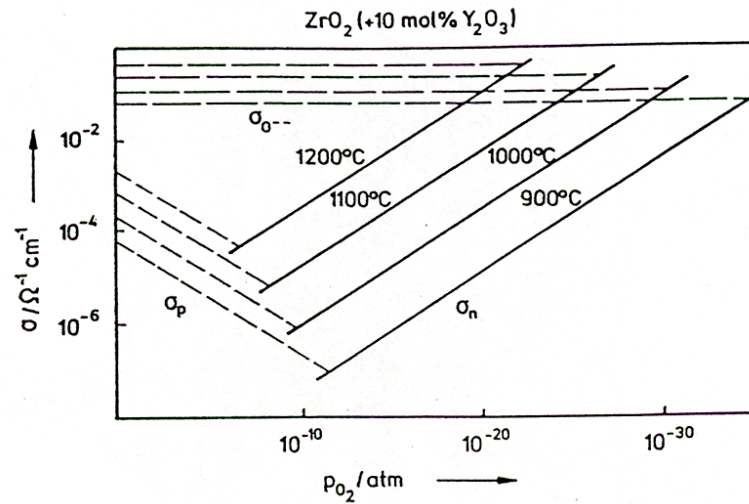
Electrical Neutrality

$$n + [V_M'] = p + [V_X^\bullet] + [D_M^\bullet]$$

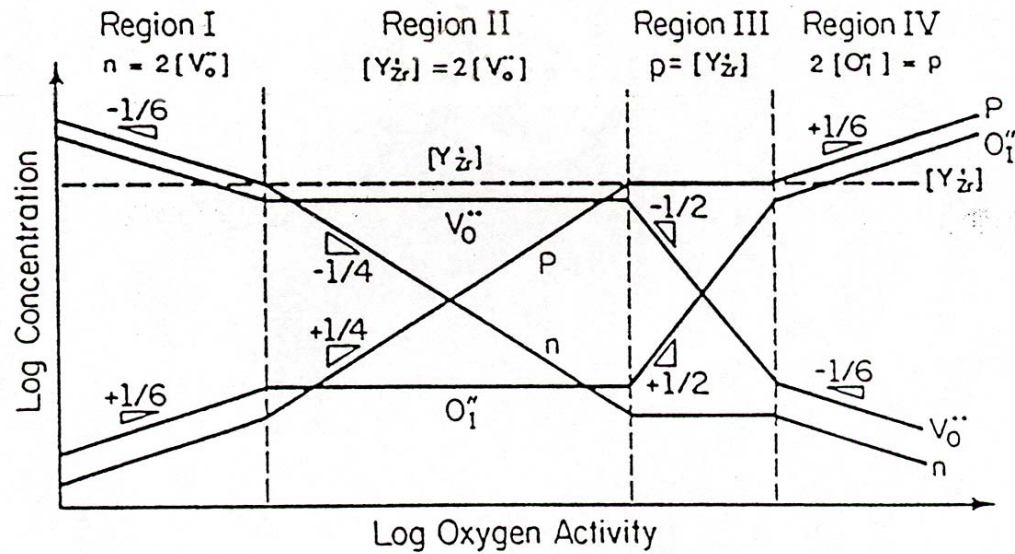
where;



The Kröger-Vink diagram for donor-doped MX with the parameters given in the text: dashed lines, diagram for pure MX.



Partial conductivities of electrons, electron defects and oxygen ions in  $\text{ZrO}_2$  (+ 10 mol-%  $\text{Y}_2\text{O}_3$ ) at different temperatures as a function of the oxygen partial pressure



The defect concentration dependence on oxygen activity in YSZ.



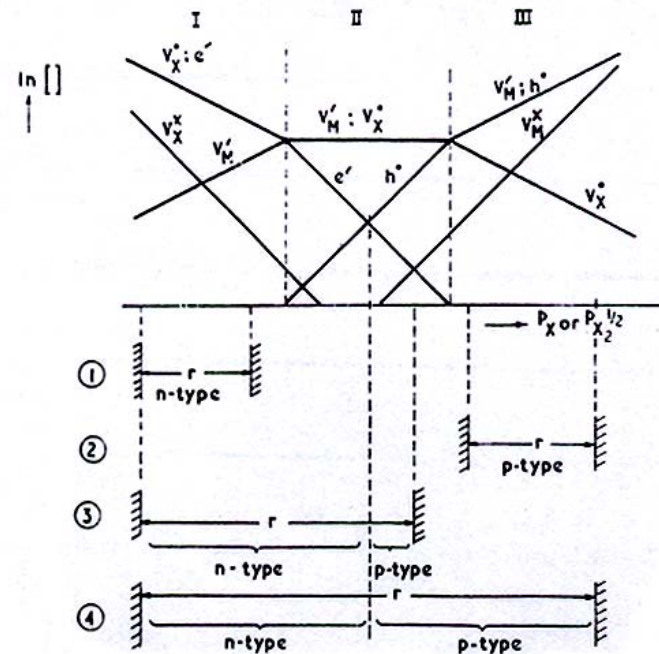
# Compositional Gradients

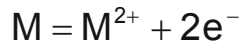
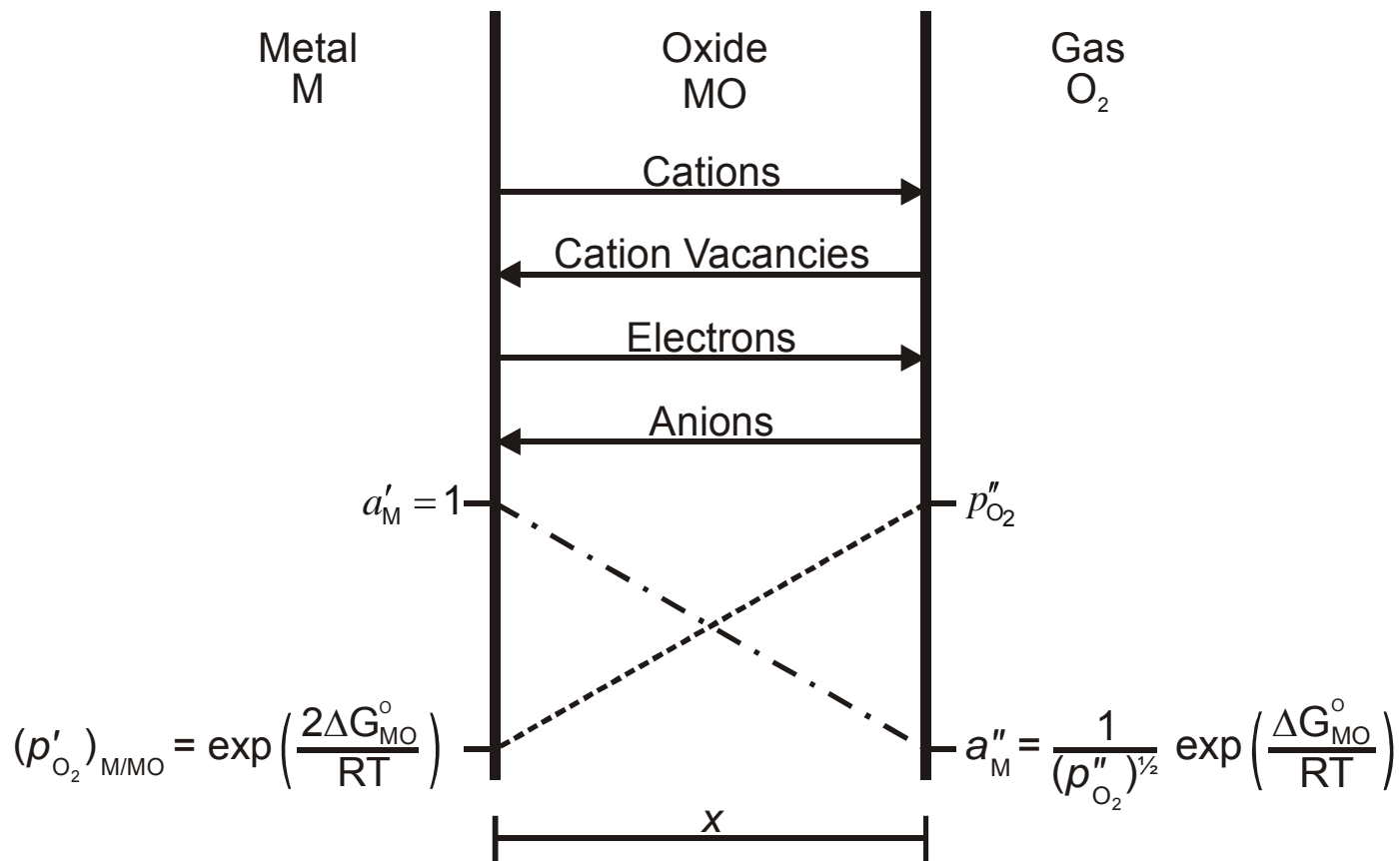
- The diagram shows various possibilities for the dependence of basic imperfections on the partial pressure as found in simple ionic conductors. Other diagrams of course are possible depending upon the magnitude of constants such as  $K_i$  and  $K_s$  as well as the particle defect types. As this diagram indicates situations (1) and (2) are relatively simple but (3) and (4) show cases in which two or three ranges are present in a growing layer. When only one type of imperfection is mobile, the particle current is constant throughout the layer providing the deviations from stoichiometry are small for the compound. When two different atomic imperfections are involved the fluxes of these imperfections need no longer be constant through the layer. For such cases considering  $V'_M$  and  $V^\circ_X$  as the diffusing species, when:

$$\frac{dJ_{V_{M'}}}{dx} \neq 0 \quad \frac{dJ_{V_X^\bullet}}{dx} \neq 0$$

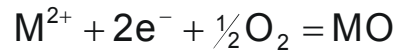
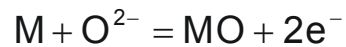
then we must have:

$$\frac{dJ_{V_{M'}}}{dx} = \frac{dJ_{V_X^\bullet}}{dx}$$

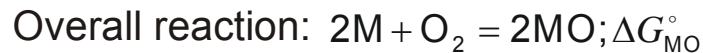
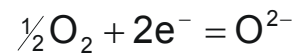




or



or



# Flux of Species due to Gradient in the Electrochemical Potential

$$j_i = -L_i \left( \frac{\partial \mu_i}{\partial X} + Z_i F \frac{\partial \phi}{\partial X} \right)$$

$J_i$ : moles/cm<sup>2</sup>sec

$Z_i$ : charge on species i

$X$ : oxide thickness

$F$ : Faraday's constant

$\mu_i$ : chemical potential

$\phi$ : electrical potential

$L_i$ : Parameter containing  $D_i$  (diffusion coefficient) or  $\kappa_i$  (conductivity)

Cation: 
$$J_1 \left( \frac{eq}{cm^2 - s} \right) = Z_1 j_1 = -\frac{\kappa_1}{Z_1 F^2} \left( \frac{\partial \mu_1}{\partial X} + Z_1 F \frac{\partial \phi}{\partial X} \right)$$

Anion: 
$$J_2 = |Z_2| j_2 = -\frac{\kappa_2}{|Z_2| F^2} \left( \frac{\partial \mu_2}{\partial X} - |Z_2| F \frac{\partial \phi}{\partial X} \right)$$

Electrons: 
$$J_3 = j_3 = -\frac{\kappa_3}{F^2} \left( \frac{\partial \mu_3}{\partial X} - F \frac{\partial \phi}{\partial X} \right) = -\frac{\kappa_3}{F^2} \frac{\partial \eta_3}{\partial X}$$

For the oxide to stay locally electrically neutral,

$$J_1 + |J_2| = J_3$$

The parabolic rate constant defined as:

$$\Delta x^2 = 2kt$$

For an electronic conductor

$$k = \int_{a'_0}^{a''_0} \left( \frac{Z_1}{|Z_2|} D_1 + D_2 \right) d \ln a_0$$

or

$$k = -\frac{\tilde{V}}{F^2} \int_{\mu'_M}^{\mu''_M} \frac{\kappa_1 + \kappa_2}{Z_1} d\mu_M$$

For an ionic conductor

$$k = \frac{RT\tilde{V}}{F^2} \int_{a'_0}^{a''_0} \left( \frac{\kappa_3}{|Z_2|} \right) d \ln a_0$$

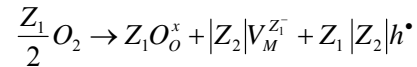
$$a_O \equiv P_{O_2}^{1/2} (atm)$$

$\tilde{V}$  = equivalent volume

# The Parabolic Rate Constant in Terms of Defect Concentrations

$Z_1$  and  $Z_2$  can be related to the oxide composition for electrical neutrality  $|Z_2|M^{Z_1}=Z_1O^{[Z_2]}$ . Hence,

$M_{|Z_2|}O_{Z_1}$ , or  $MO_{(Z_1/Z_2)}$   
for incorporation of  $O_2$  into  $MO_{(Z_1/Z_2)}$



Upon applying the law of mass action to the above expression and satisfying the electrical neutrality condition

$$d \ln a_o = \frac{|Z_2|(1+Z_1)}{Z_1} d \ln [V_M^{Z_1^-}]$$

Substituting into the previous expression for k where  $D_1 \gg D_2$

$$k = \frac{\left[ V_M^{Z_1^-} \right]''}{\left[ V_M^{Z_1^-} \right]'} \int (1+Z_1) D_1 d \ln [V_M^{Z_1^-}]$$

For cation diffusing via a vacancy mechanism

$$D_1 = [V_M^{Z_1^-}] D_{V_M^{Z_1^-}}$$

$$k = (1+Z_1) \int_{\left[ V_M^{Z_1^-} \right]'}^{\left[ V_M^{Z_1^-} \right]''} D_{V_M^{Z_1^-}} dV_M^{Z_1^-}$$

Assuming  $D_{V_M^{Z_1^-}}$  is constant

$$k = (1 + Z_1) D_{V_M^{Z_1^-}} \left[ \left[ V_M^{Z_1^-} \right]'' - \left[ V_M^{Z_1^-} \right] \right]$$

For p-type oxides  $\left[ V_M^{Z_1^-} \right]'' \gg \left[ V_M^{Z_1^-} \right]$

$$k = (1 + Z_1) D_{V_M^{Z_1^-}} \left[ V_M^{Z_1^-} \right]''$$

$$k = (1 + Z_1) D_1''$$

Where  $D_1''$  is the value of  $D_1$  at the  $MX_{\frac{Z_1}{|Z_2|}}$ -gas interface

In case of n-type compound

$$k = (1 + Z_1) D_1' \quad \text{where } D_1' \text{ is the value of } D_1 \text{ at the } M - MX_{\frac{Z_1}{|Z_2|}} \text{ interface.}$$

# Electrical Conduction

$$\sigma_n = pe\mu_n$$

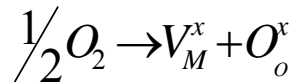
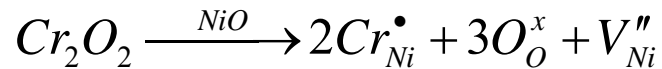
$$\sigma_e = ne\mu_e$$

$\sigma_n, \sigma_e$       electrical conductivity via holes or electrons

$p, n$           concentration of holes or electrons

$\mu_h, \mu_e$       mobility of holes or electrons

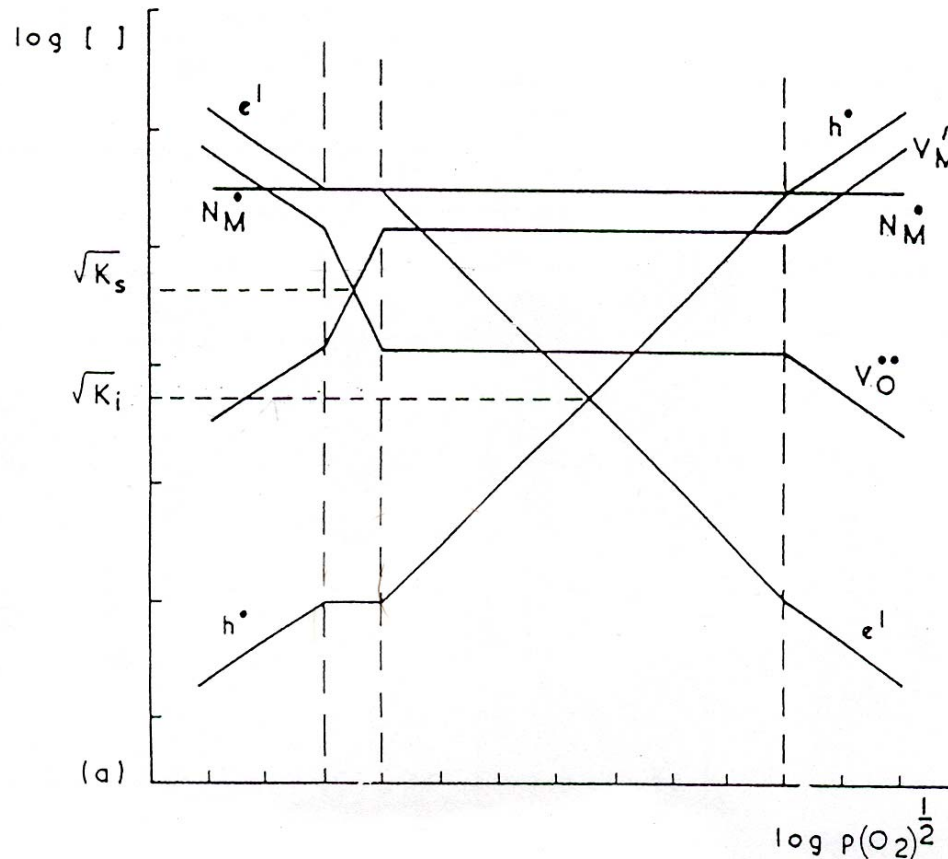
Consider  $\text{Cr}_2\text{O}_3$  added to NiO with Schottky Defects



Applying law of mass action

$$K = \text{const.} = \frac{[V_{\text{M}}'']p^2}{P_{\text{O}_2}^{1/2}}$$

# Kröger-Vink Diagram Applicable to $\text{Cr}_2\text{O}_3$ Addition to NiO with Schottky Defects



1. For  $[\text{Cr}_{\text{Ni}}^\circ] = 2[\text{V}_{\text{Ni}}^{\bullet\bullet}]$  and constant  $P(\text{O}_2)$  as increase  $\text{Cr}_2\text{O}_3$  in solution in NiO,  $[\text{Cr}_{\text{Ni}}^\circ]$  and  $[\text{V}_{\text{Ni}}^{\bullet\bullet}]$  increase,  $p$  decreases.
2. If dope with a fixed amount of  $\text{Cr}_2\text{O}_3$  and  $[\text{Cr}_{\text{Ni}}^\circ] = 2[\text{V}_{\text{Ni}}^{\bullet\bullet}]$ ,  $p$  increases as  $P(\text{O}_2)$  increases.
3. If  $p = 2[\text{V}_{\text{Ni}}^{\bullet\bullet}]$  the concentration of  $\text{Cr}_2\text{O}_3$  is too low to affect  $[\text{V}_{\text{Ni}}^{\bullet\bullet}]$  and  $p$  and they increase with  $P(\text{O}_2)$ .

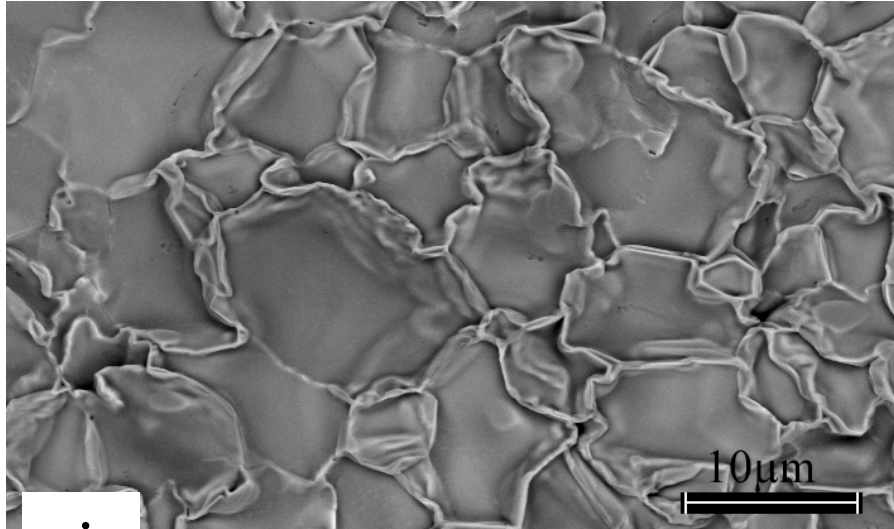


# Growth of Oxides on Pure Metals

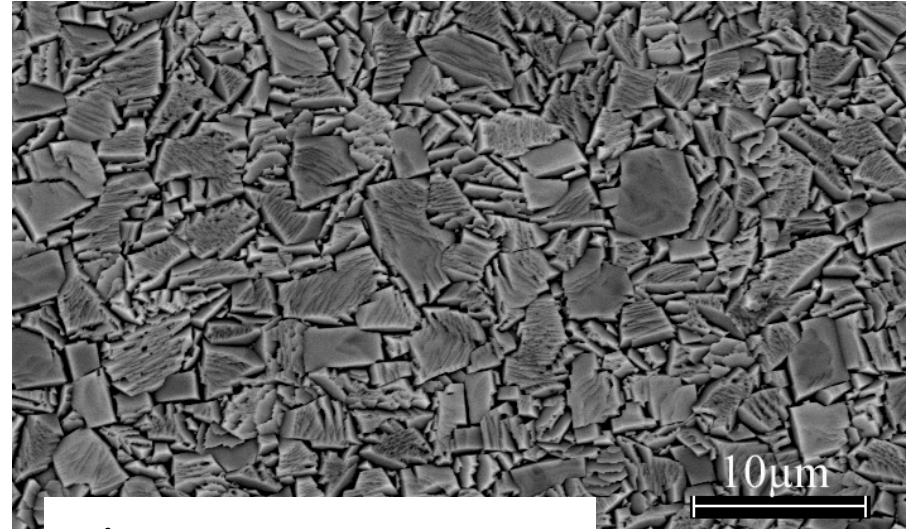
Focus on Diffusion-Controlled Growth

1. Simple Parabolic Oxidation Model
2. Effect of Oxygen Partial Pressure
3. Bulk vs. Grain Boundary Diffusion

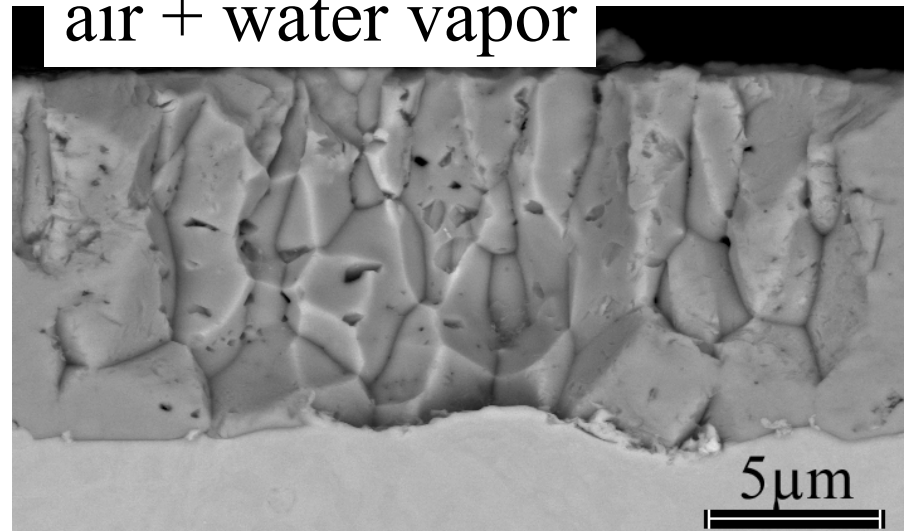
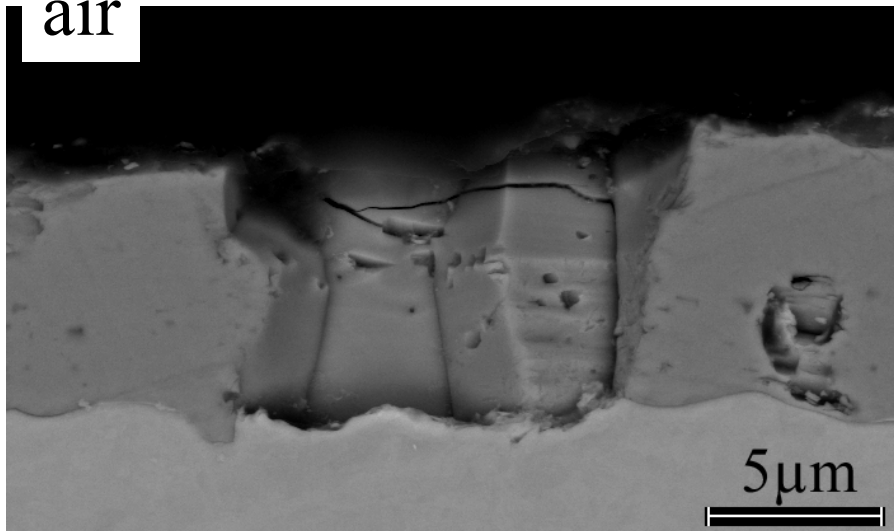
# Pure Ni exposed for 1 hour @ 1100°C

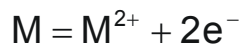
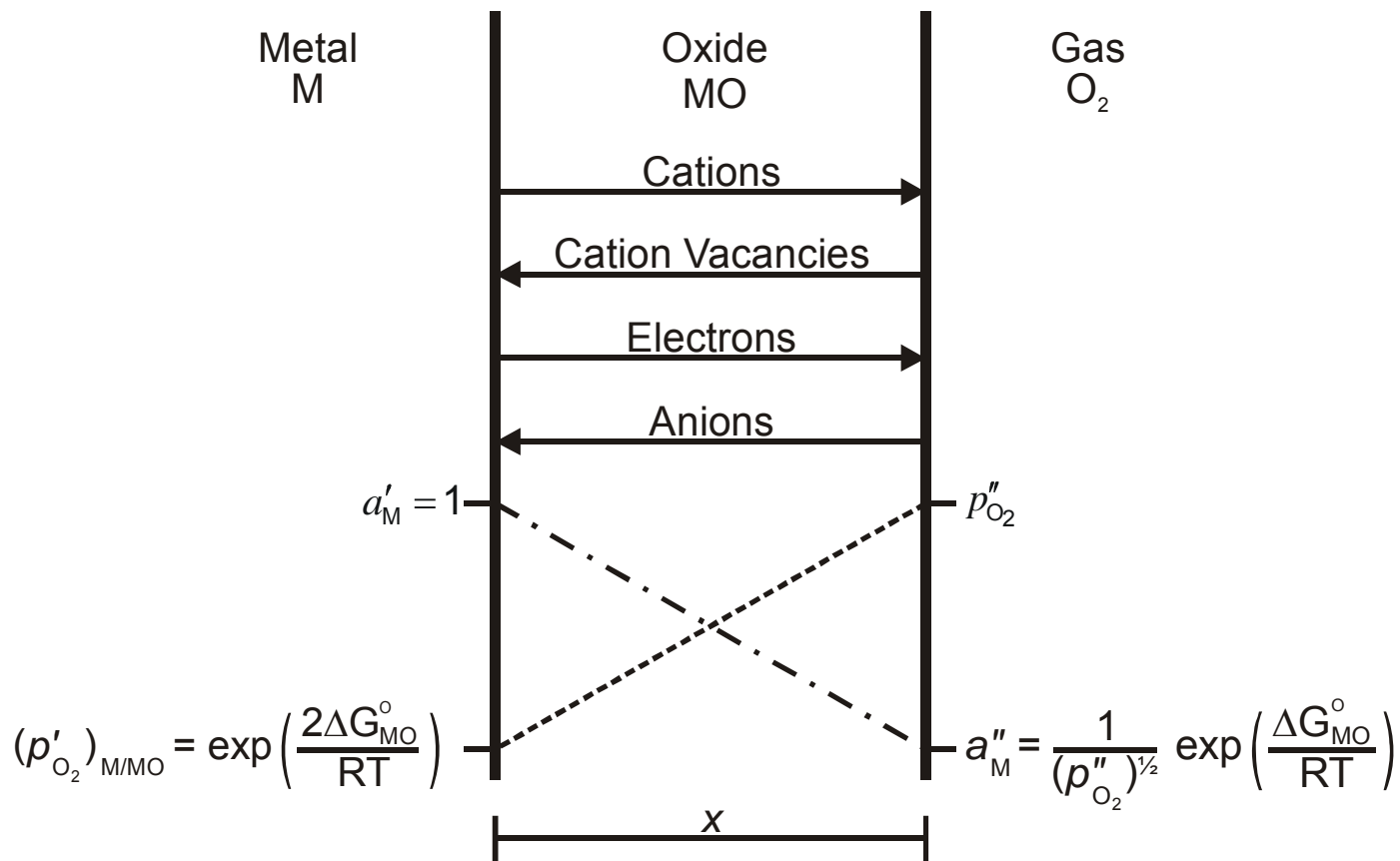


air

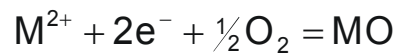
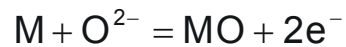


air + water vapor

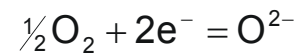




or



or



# Simplified Treatment of Diffusion-Controlled Oxidation

$$j_{M^{2+}} = -j_{V_M} = D_{V_M} \frac{C_{V_M}'' - C_{V_M}'}{x}$$

$$j_{M^{2+}} = \frac{1}{V_{ox}} \frac{dx}{dt} = D_{V_M} \frac{C_{V_M}'' - C_{V_M}'}{x}$$

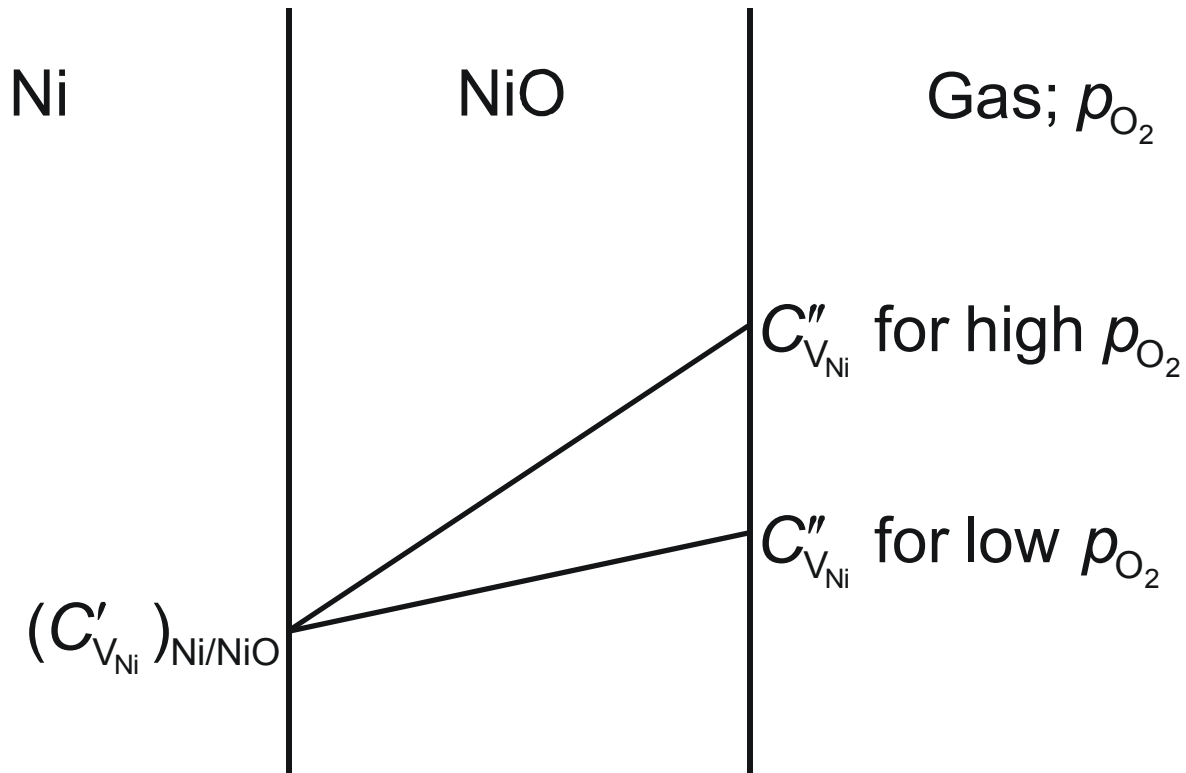
$$\frac{dx}{dt} = \frac{k'}{x}$$

$$k' = D_{V_M} V_{ox} (C_{V_M}'' - C_{V_M}')$$

$$x^2 = 2k't$$

## Effect of oxygen partial pressure

(p-type oxide)



# Effect of oxygen partial pressure

$$\frac{1}{2} O_2 = O_o + h\dot{ } + V_{Co}'$$

$$C_{h\dot{ }} C_{V_{Co}}'' = K p_{O_2}^{1/2}$$

$$C_{h\dot{ }} = C_{V_{Co}}'$$

$$C_{V_M} = \text{const.} p_{O_2}^{1/4}$$

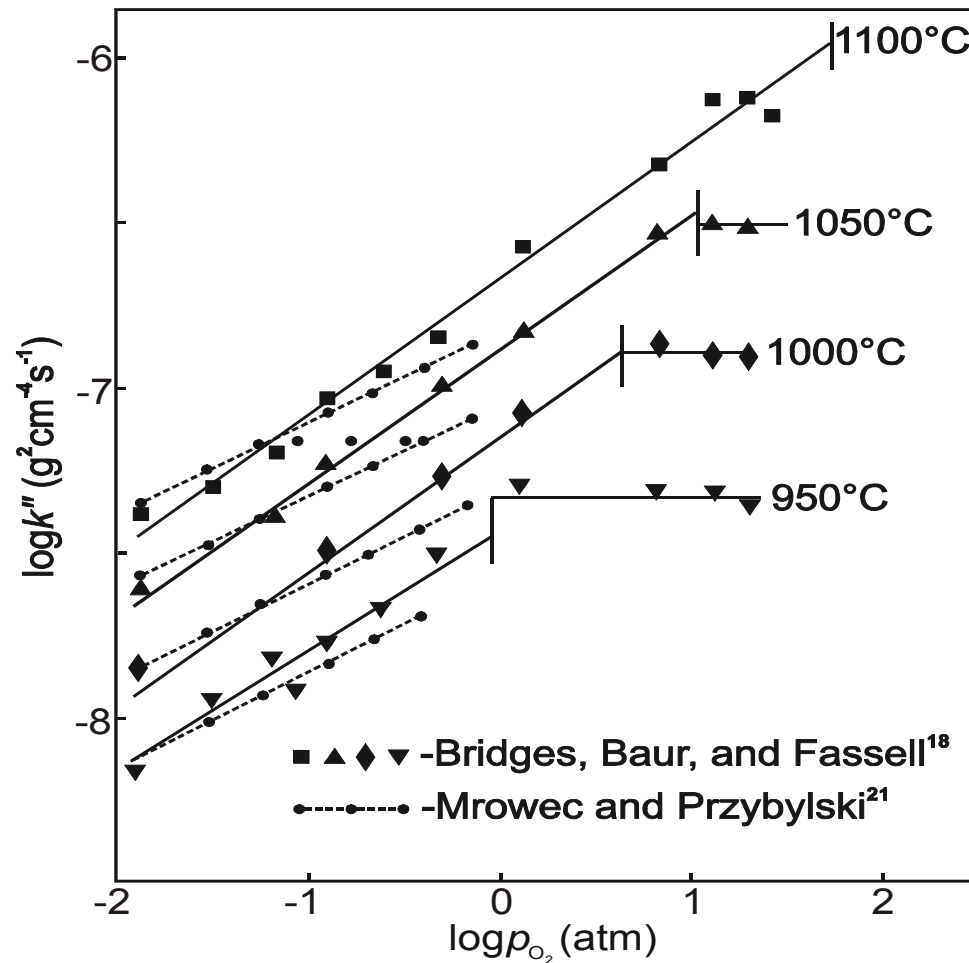
$$C_{V_M} = \text{const.} p_{O_2}^{1/n}$$

$$k' \propto \left[ \left( p_{O_2}'' \right)^{1/n} - \left( p_{O_2}' \right)^{1/n} \right]$$

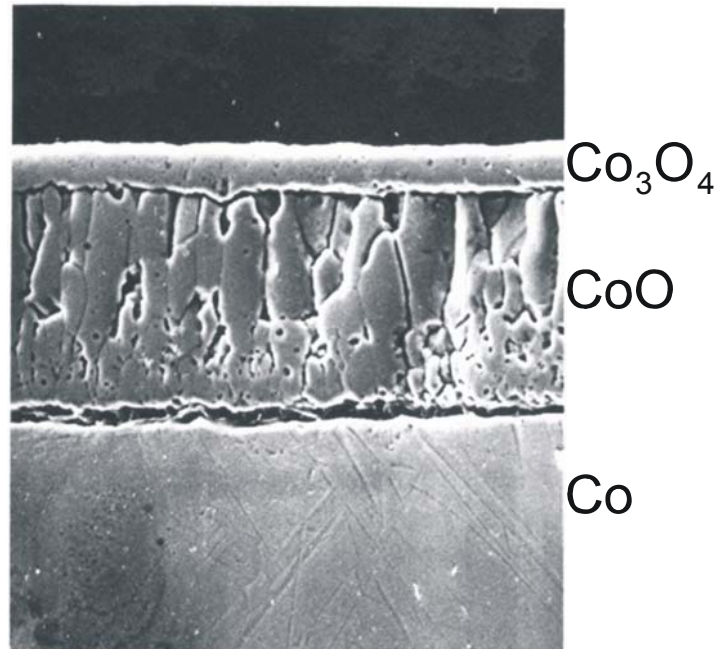
$$k' \propto \left( p_{O_2}'' \right)^{1/n}$$

# Effect of oxygen partial pressure

## Oxidation of Co

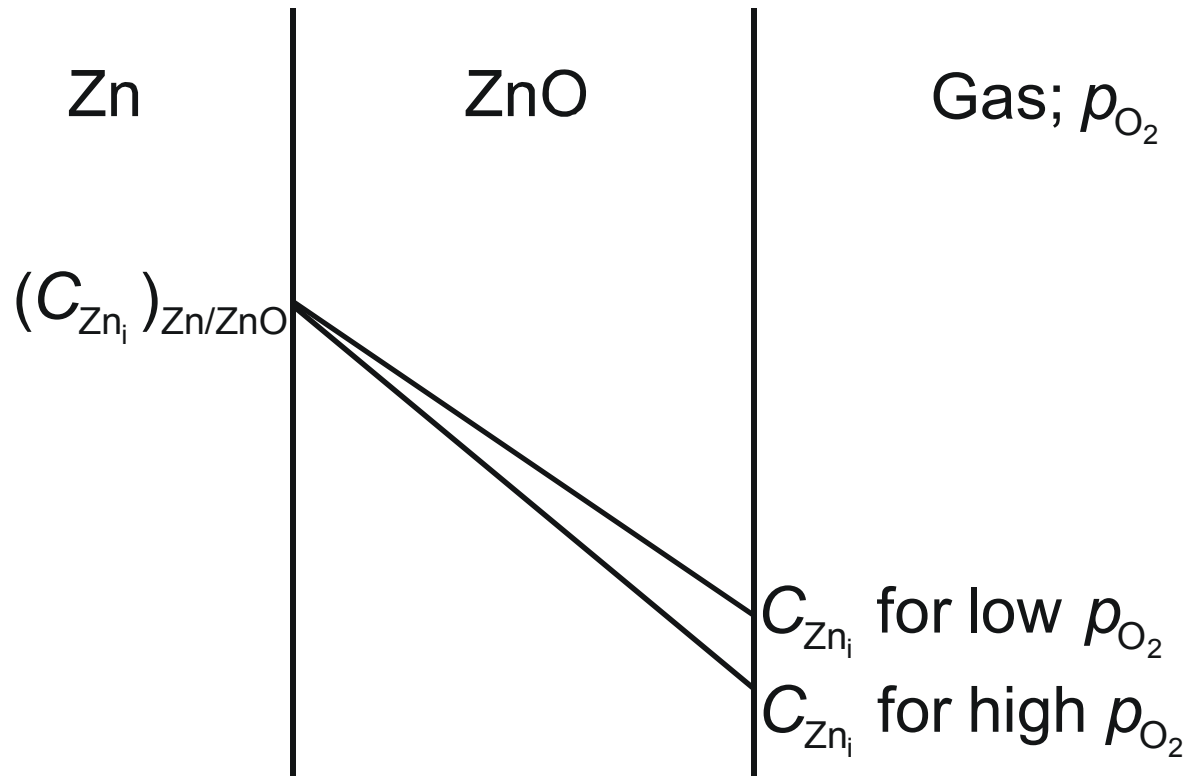


# Cross-section of Co oxidized in Air at 750°C





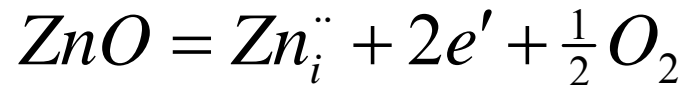
# Effect of oxygen partial pressure (n-type oxide)



# Effect of oxygen partial pressure

$$j_{M^{2+}} = \frac{1}{V_{ox}} \frac{dx}{dt} = D_{M_i} \frac{C'_{M_i} - C''_{M_i}}{x}$$

$$k' = D_{M_i} V_{ox} (C'_{M_i} - C''_{M_i})$$



$$K_1' = C_{Zn_{\dot{i}}} C_{e'}^2 p_{O_2}^{1/2}$$

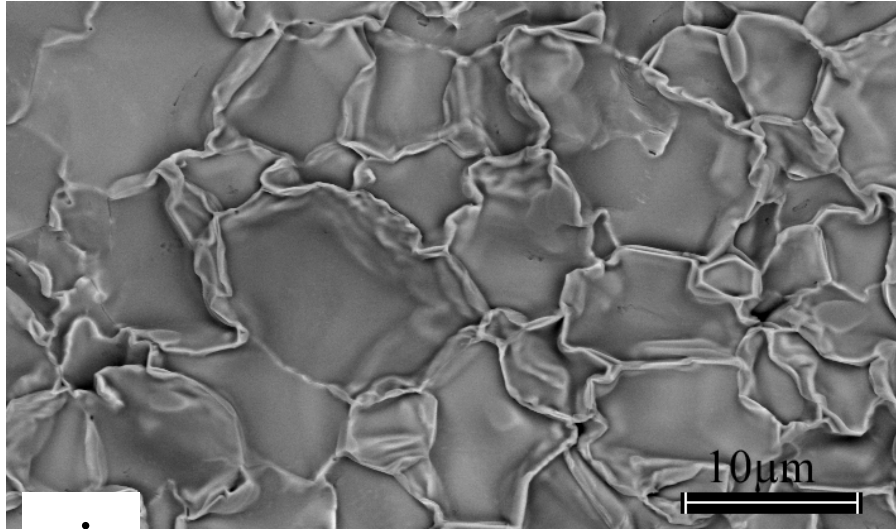
$$2C_{Zn_{\dot{i}}} = C_{e'}$$

$$K_1' = 4C_{Zn_{\dot{i}}}^3 p_{O_2}^{1/2}$$

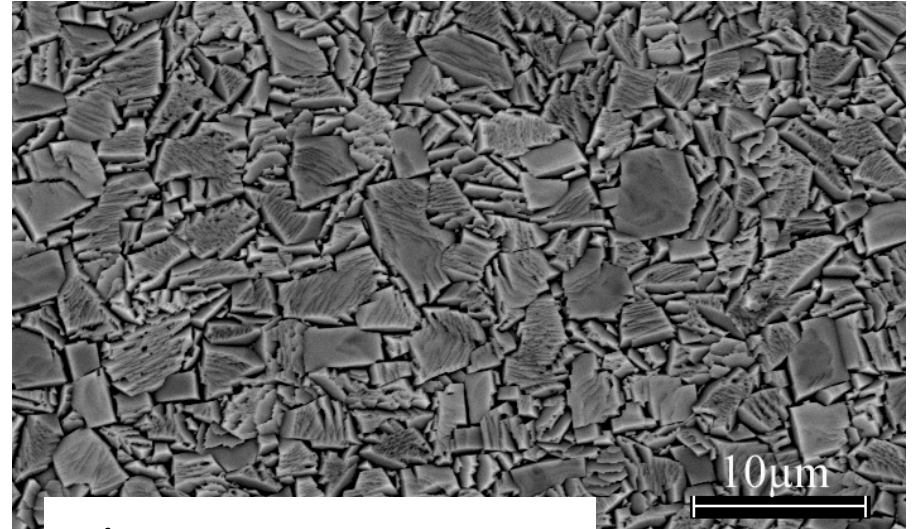
$$C_{Zn_{\dot{i}}} = \left( K_1' / 4 \right)^{1/3} p_{O_2}^{-1/6} = const. p_{O_2}^{-1/6}$$

$$k'_{ZnO} = const. \left[ \left( \frac{1}{p_{O_2}'} \right)^{1/6} - \left( \frac{1}{p_{O_2}''} \right)^{1/6} \right]$$

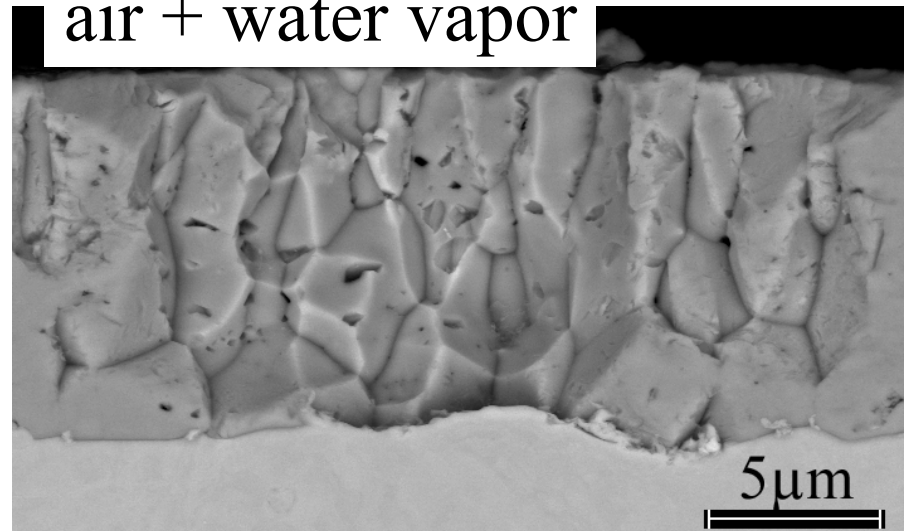
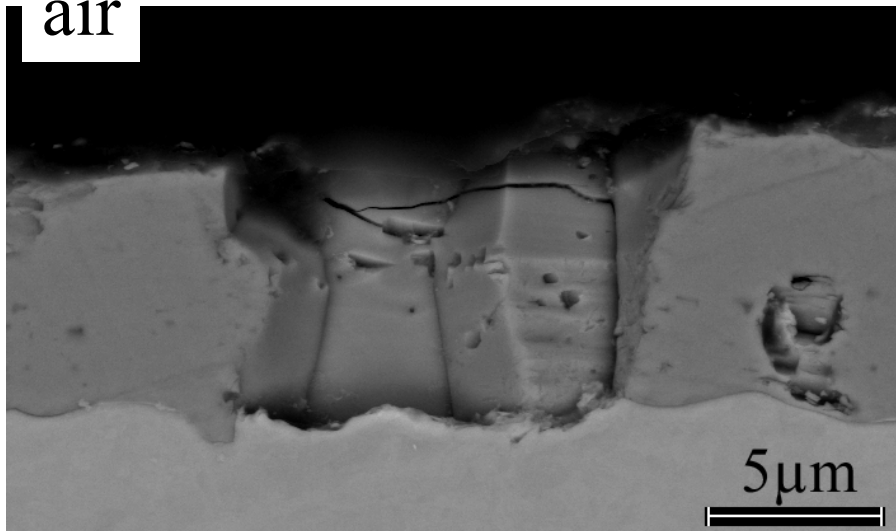
# Pure Ni exposed for 1 hour @ 1100°C



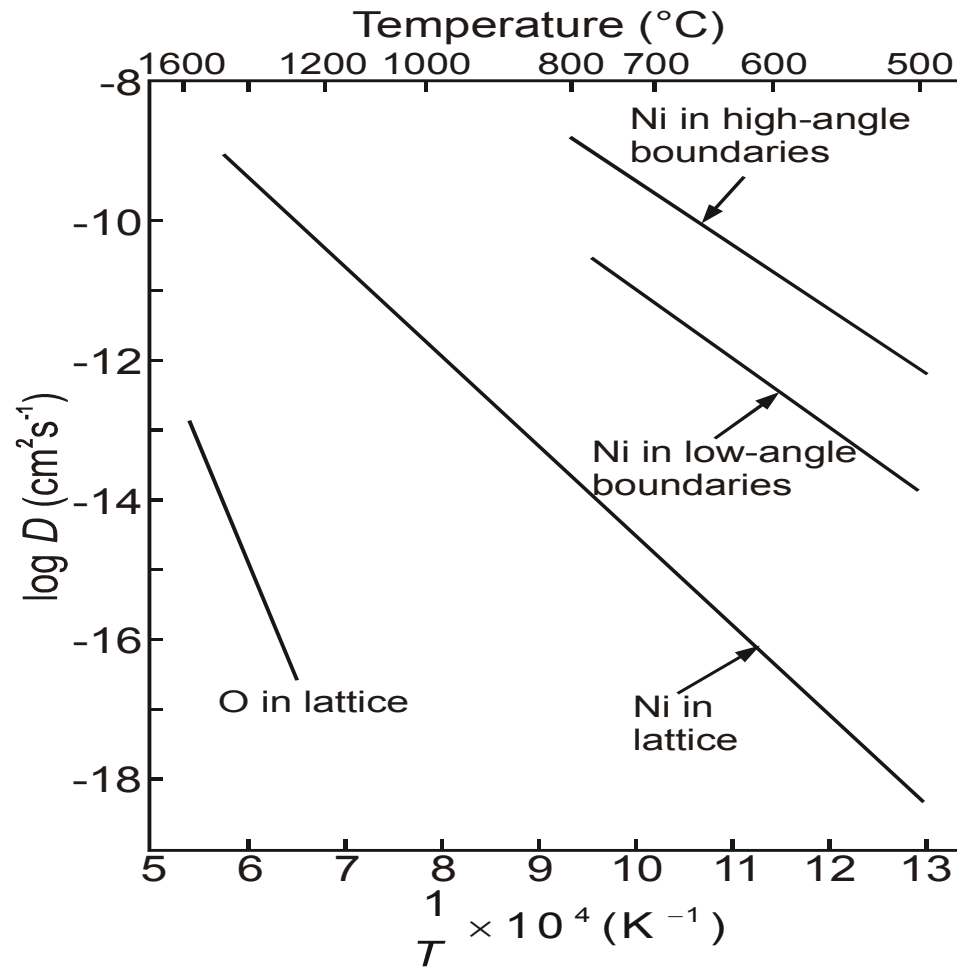
air



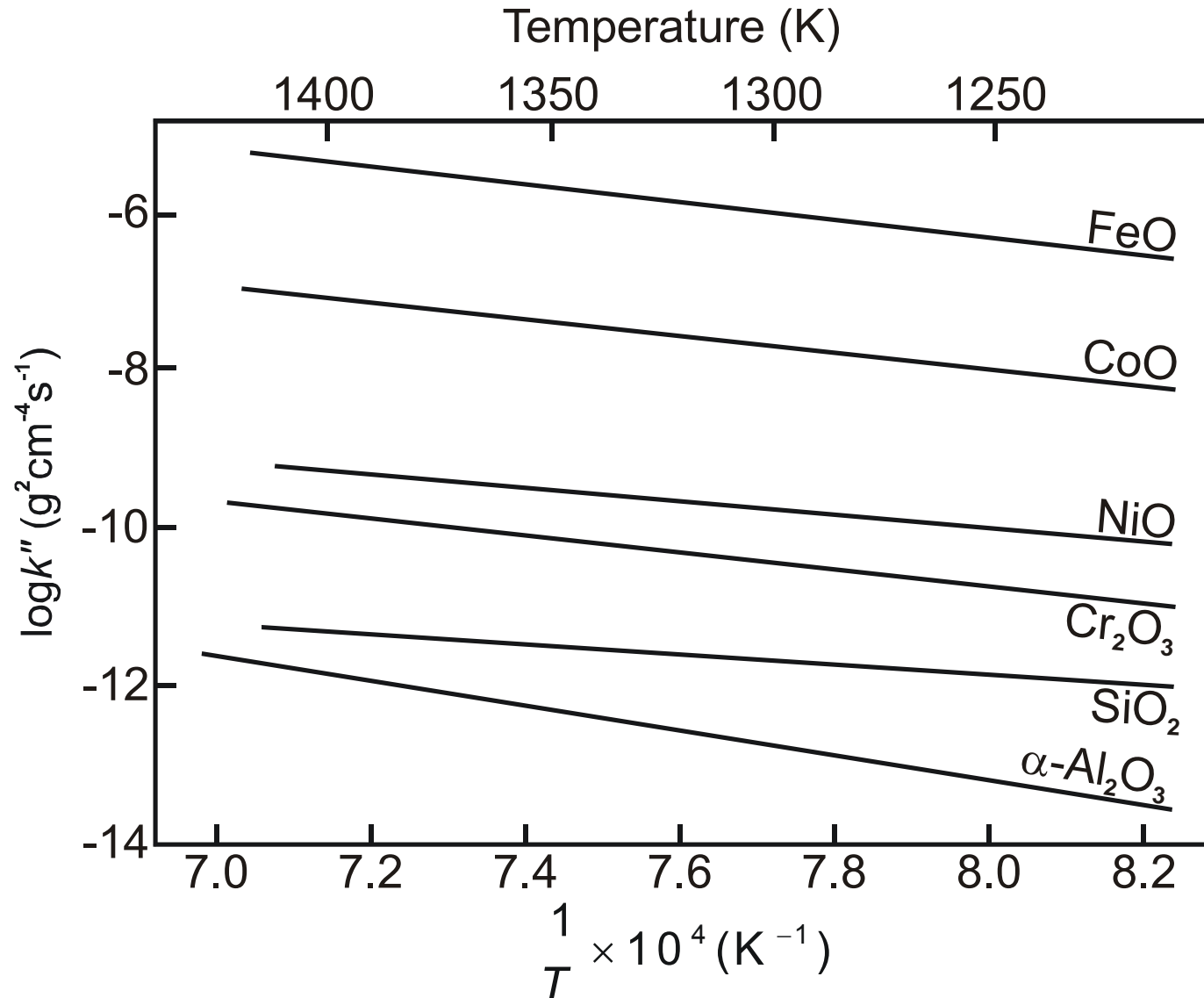
air + water vapor



# Transport Paths - NiO



# Relative growth rates of several oxides



# Selective Oxidation

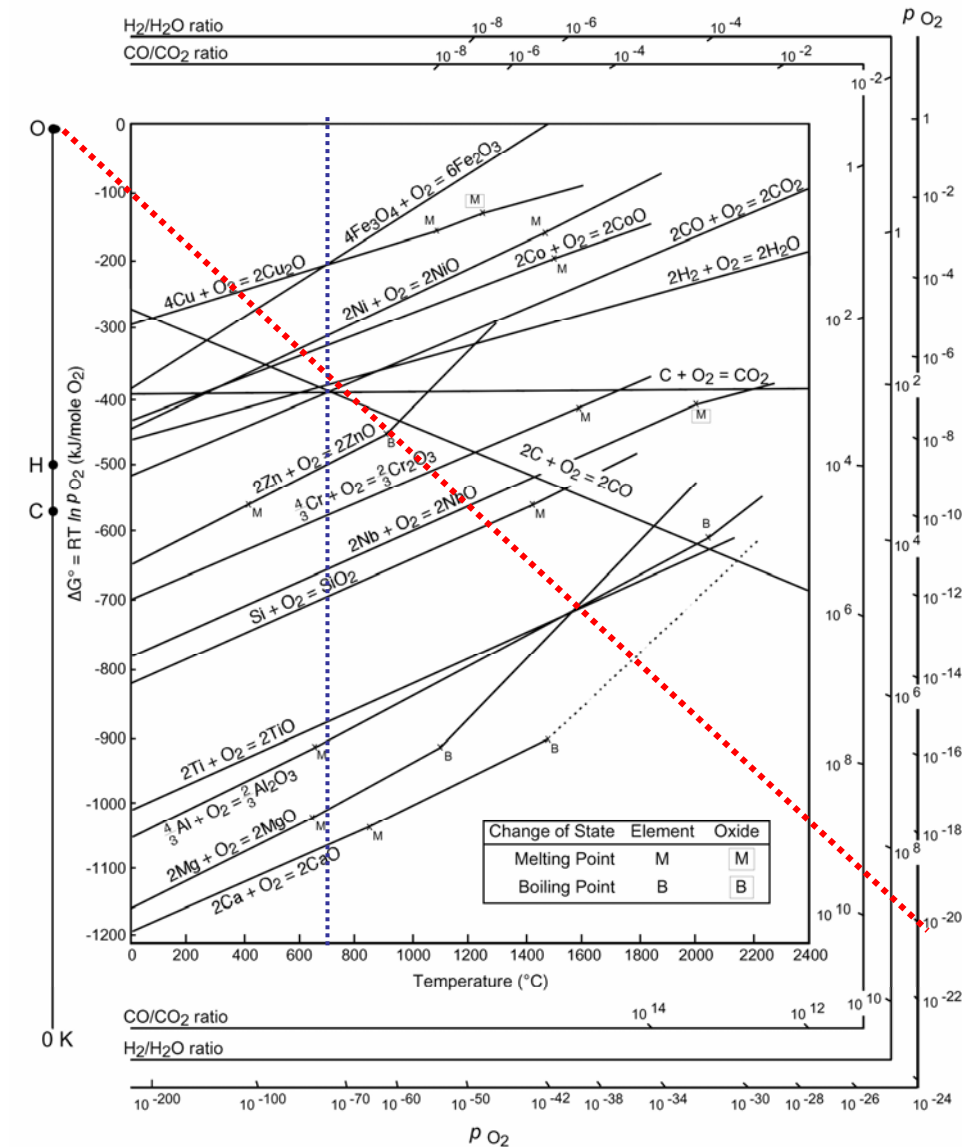
The approach to developing high temperature corrosion resistance in alloys is to have the reactants, namely the alloy and the gas, form a reaction product that separates the reactants and that allows slow transport of the reactants through it.



Most environments encountered in practice contain some oxygen, hence protective barriers are usually  $\alpha\text{-Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{SiO}_2$ .

**For SOFC-ICs one wants to avoid the selective oxidation of Si and Al.**

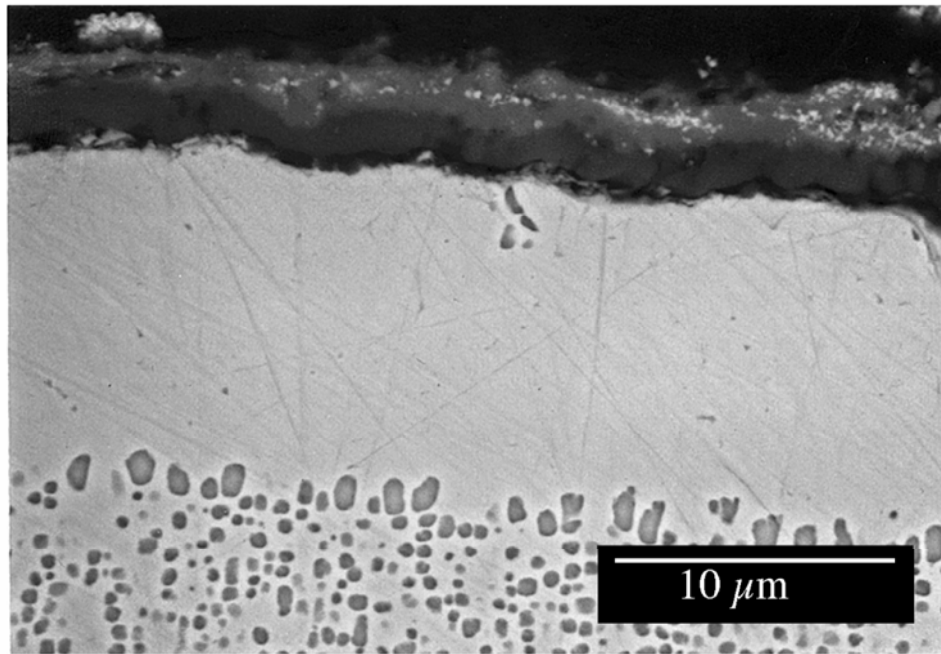
# Ellingham Diagram



# PWA 1484 oxidized at 1100°C

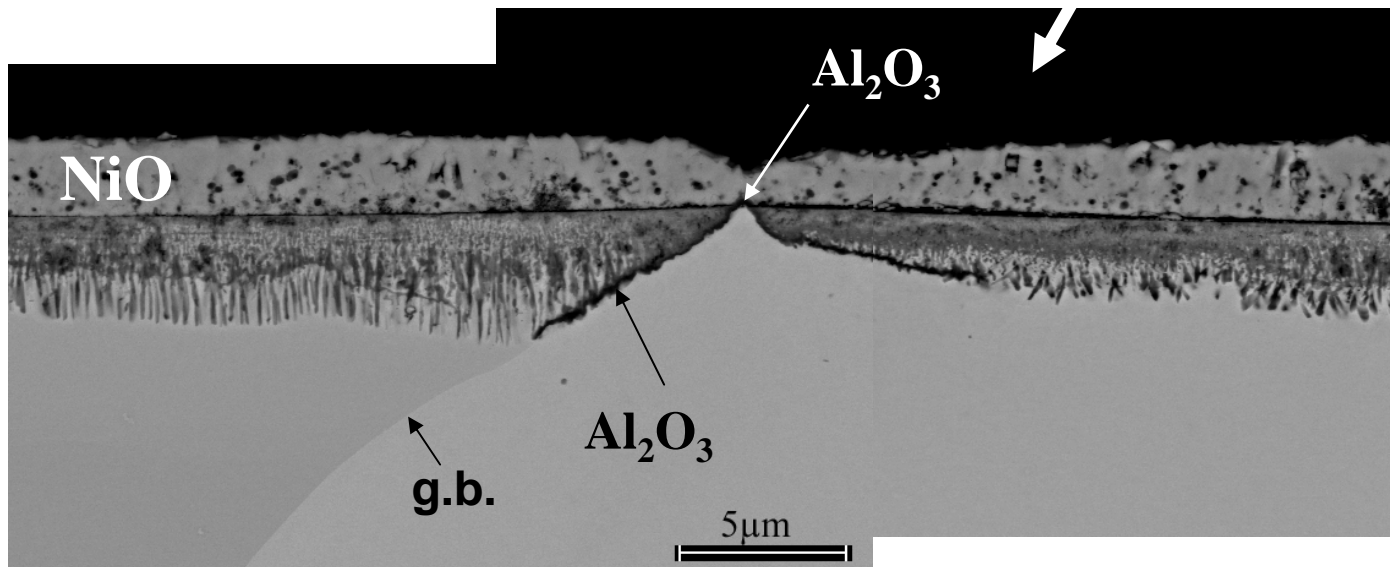
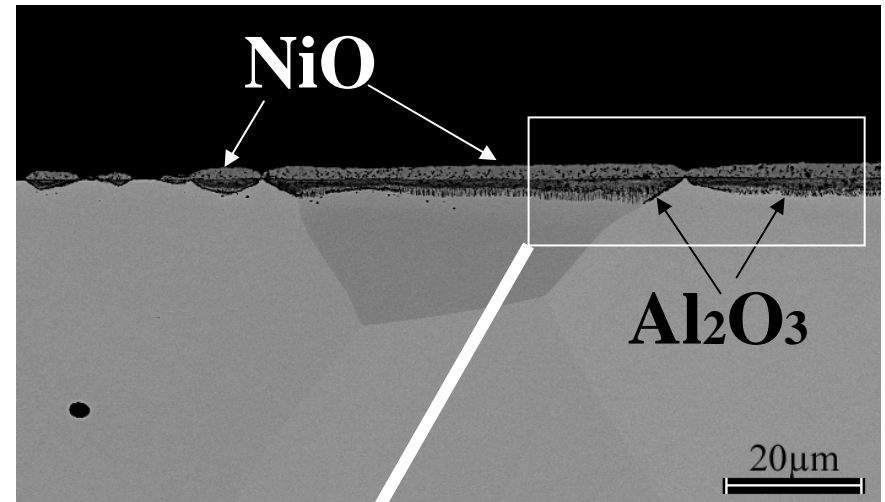
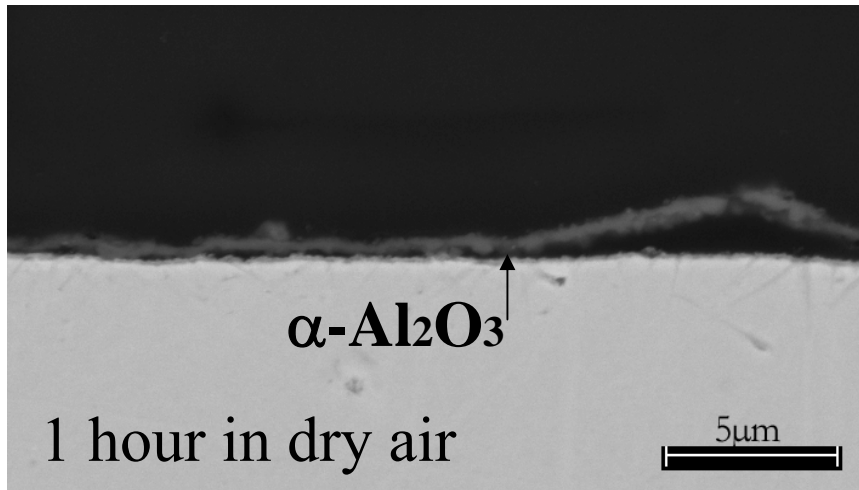
Transient  
Oxide  
Alumina

Al Depletion



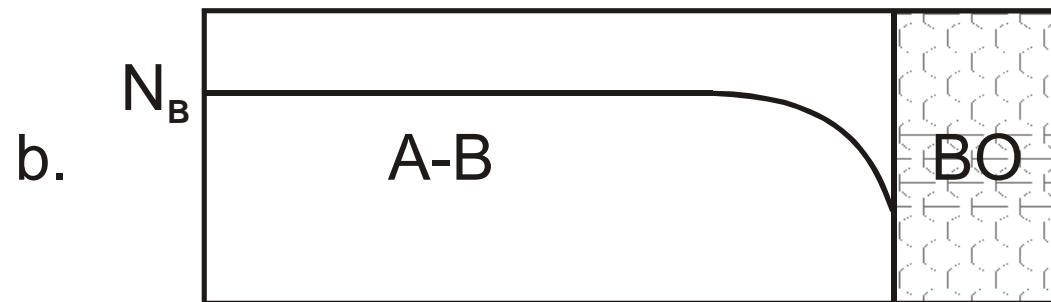
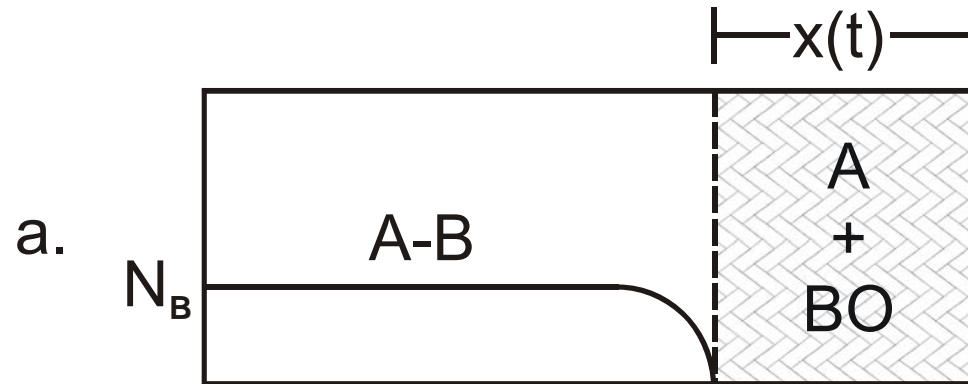


# Cross-sections of Ni-8Cr-6Al oxidized @ 1100°C



1 min in air with water vapor (0.1 atm)

# Transition to External Scale Formation



## Transition to External Scale Formation

Equating the molar fluxes of solute B and oxygen

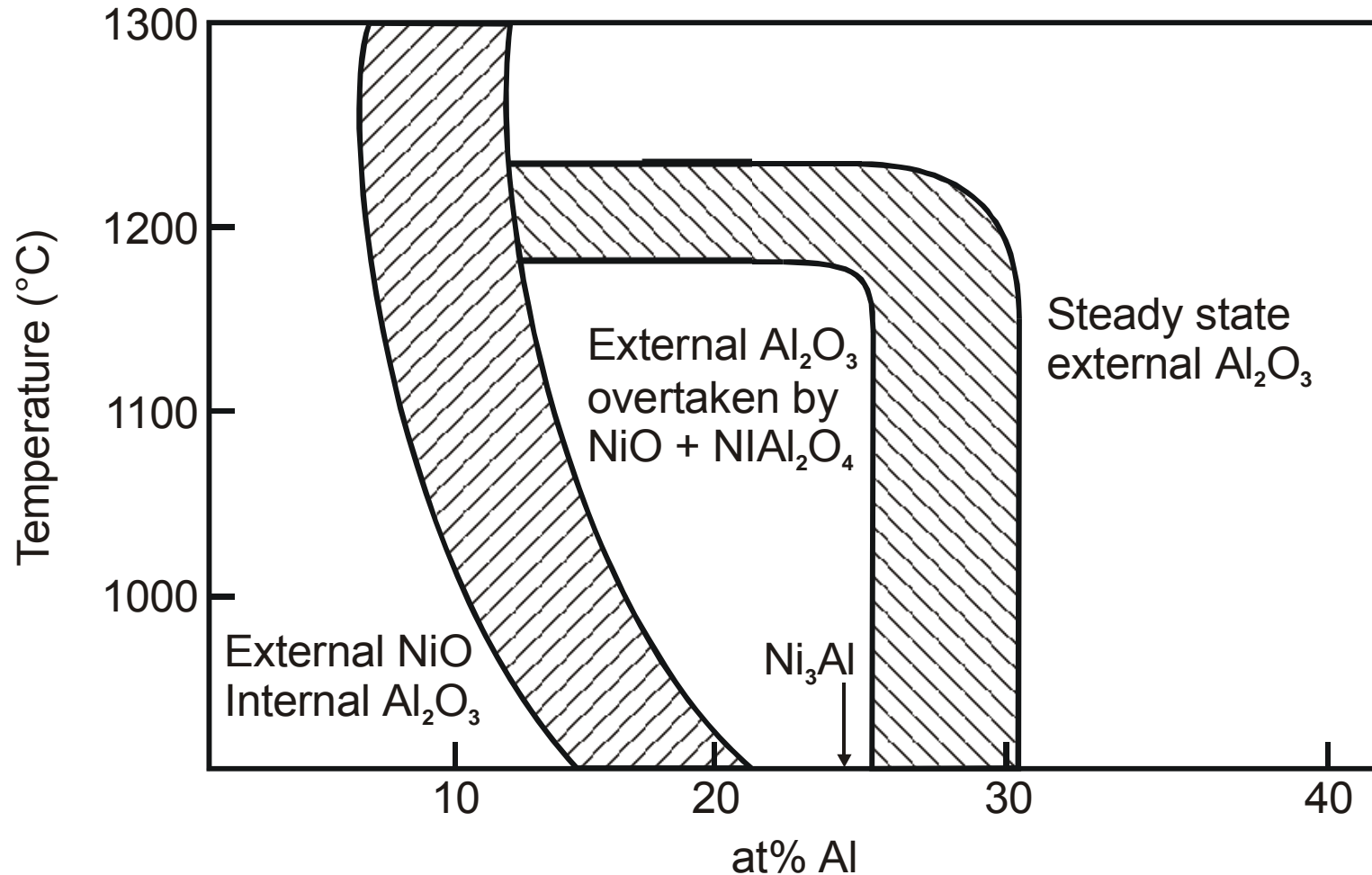
$$N_B^{(o)} > \left[ \frac{\pi g^*}{2\nu} N_O^{(s)} \frac{D_O V_m}{D_B V_{ox}} \right]^{1/2}$$

## Maintaining the Growth of an External Scale

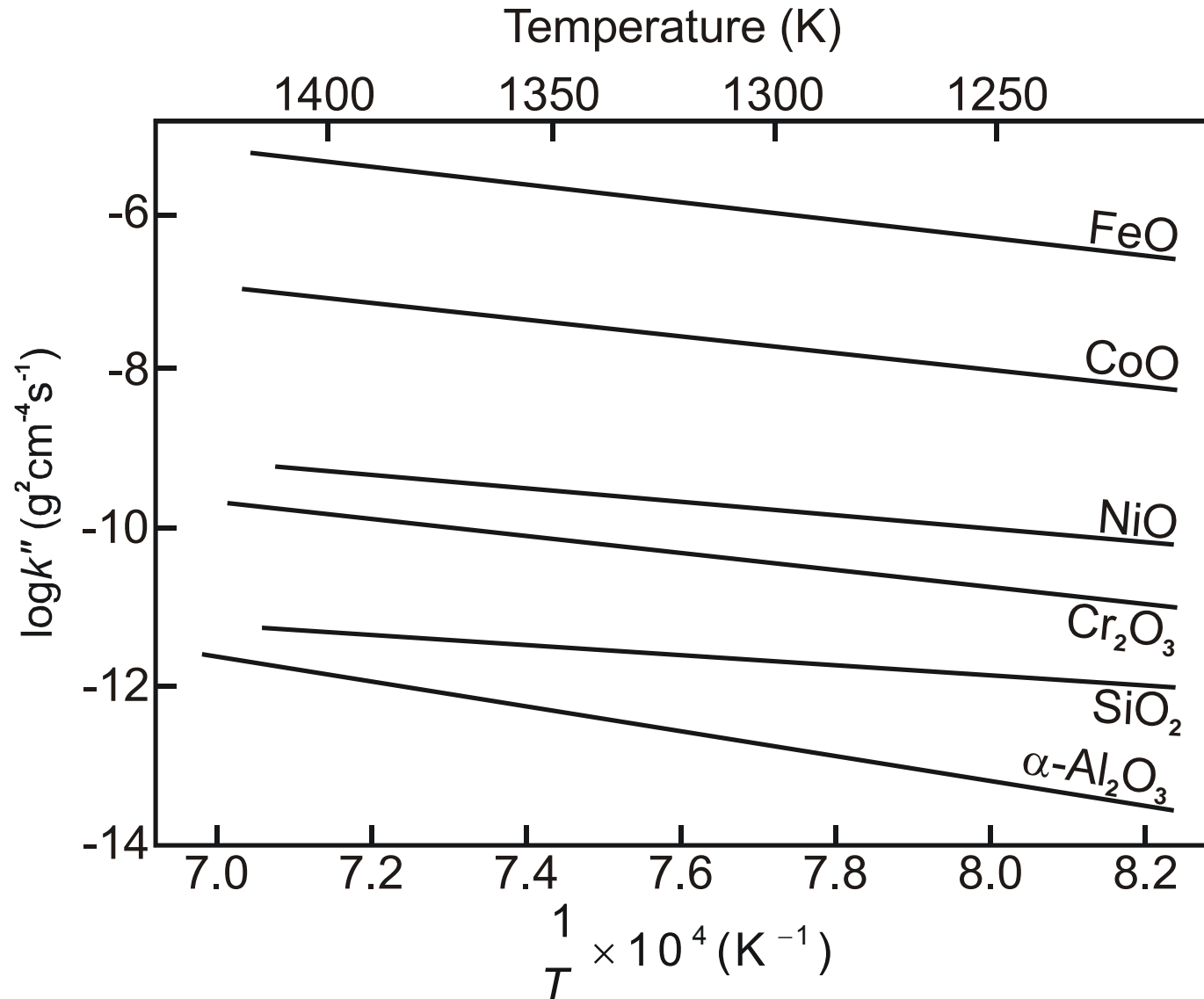
Equating the molar flux of solute B to that being required for oxide growth

$$N_B^{(o)} = \frac{V_m}{32\nu} \left( \frac{\pi k_p}{D_B} \right)^{1/2}$$

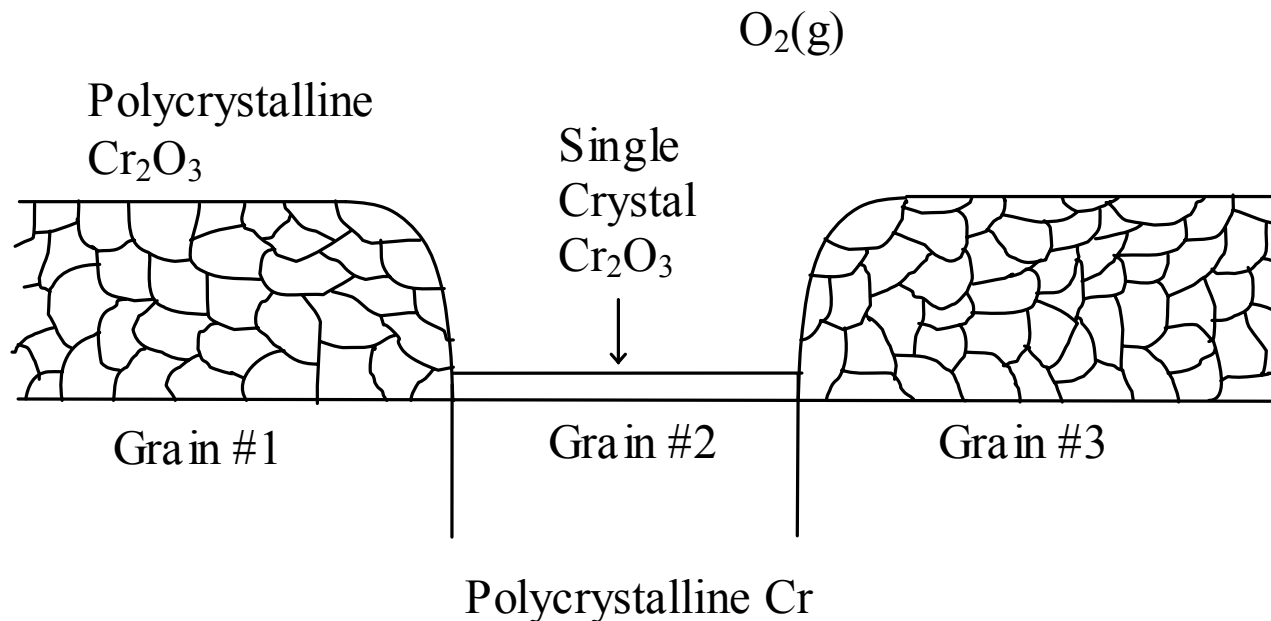
# Effect of Temperature and Al Content on the Formation and Continued Growth of External Alumina on Ni-Al Alloys



# Relative Growth Rates of Several Oxides

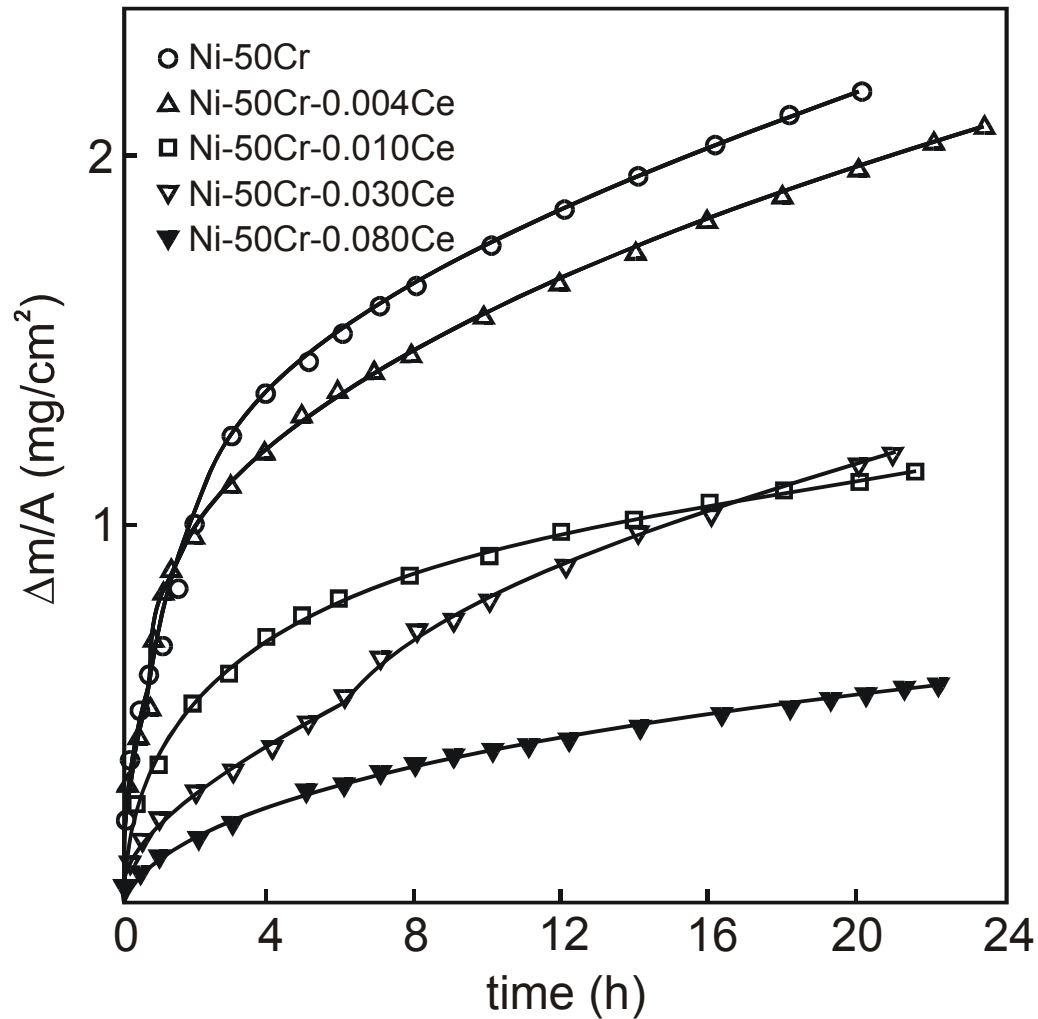


# Oxidation of Chromia-forming Alloys



Caplan and Sproule, Oxid. Of Metals, 1975

# Isothermal Oxidation – RE Effect



Ecer, and Meier, Oxid. Of Metals, 1979

Singh, Ecer, and Meier, Oxid. Of Metals, 1982

# Oxidation of Ferritic Stainless Steels

Alloy	Fe	Cr	C	Mn	Si	Ni	Mo	Ti	Al	Zr	P	S	La+Ce
Crofer	bal.	22.0	0.005	0.50	---	---	---	0.08	---	---	0.016	0.002	0.06 La
E-brite	bal.	26.0	0.001	0.01	0.025	---	1.0	---	---	---	0.020	0.020	---
26Cr Ferritic	bal.	26.0	---	~ 1.0	~ 1.0	---	1.0	---	---	---	---	---	---
AL453	bal.	22.0	0.030	0.30	0.300	---	---	0.02	0.60	---	0.020	0.030	0.10
ZMG232	bal.	22.0	0.020	0.50	0.400	0.26	---	---	0.21	0.22	---	---	0.04 La

## Exposure Conditions

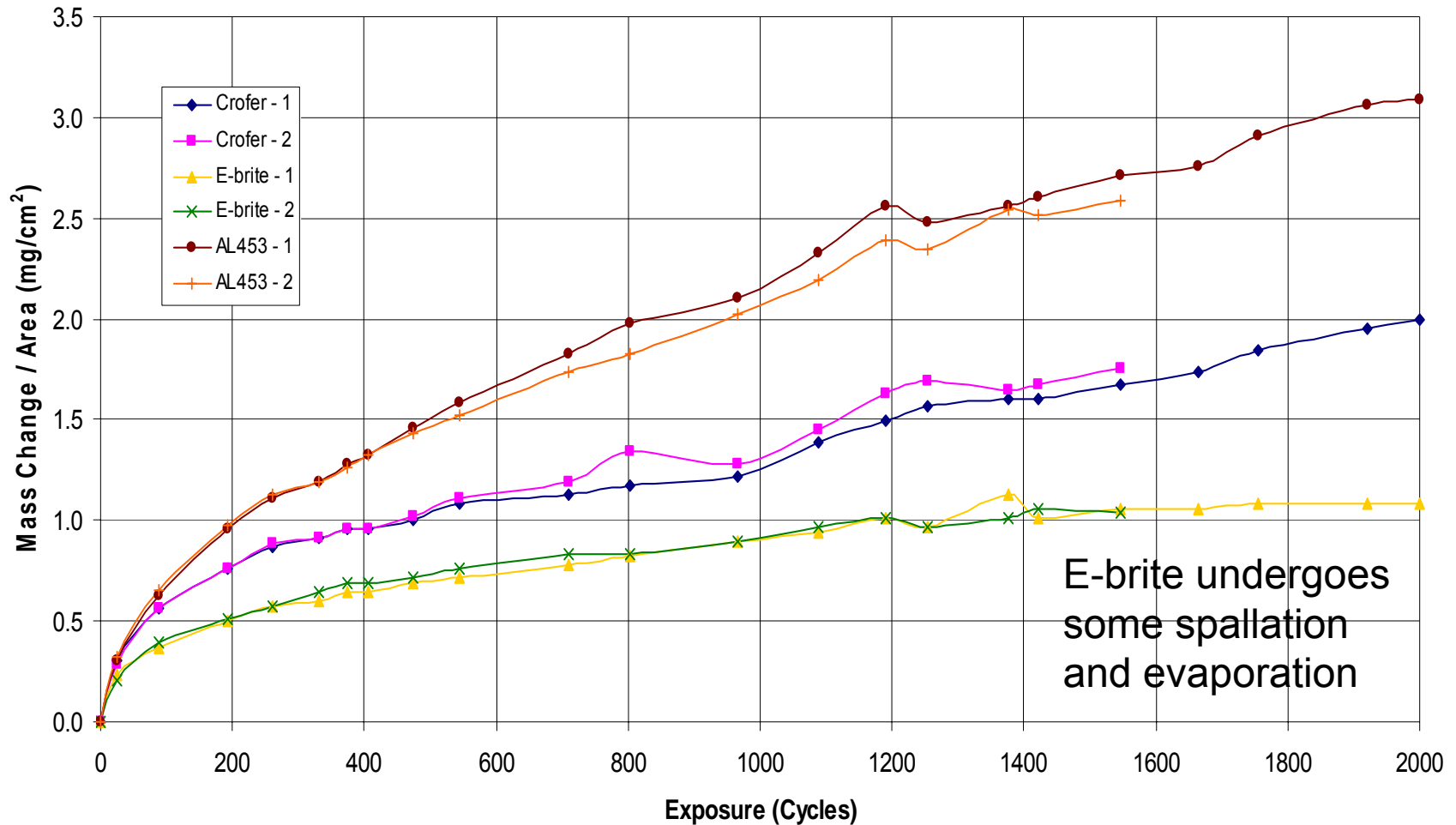
T = 700°C, 800°C, 900°C  
One-Hour Cycles

Atmosphere: Dry Air (SCG)



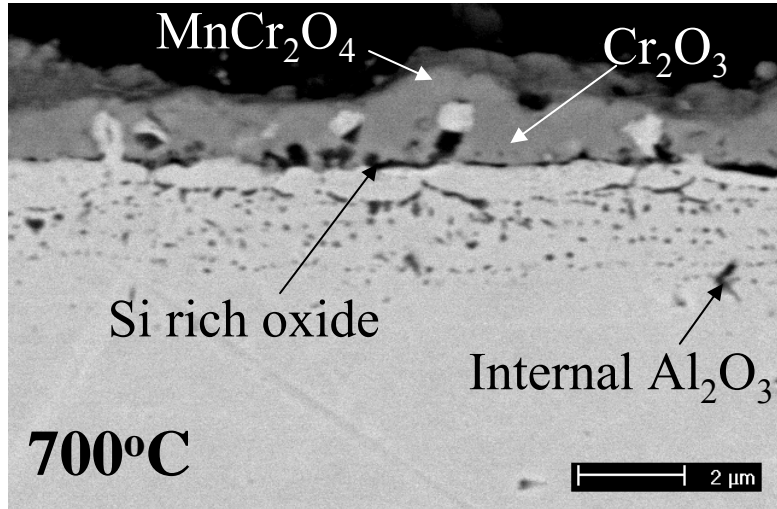
# Dry Air Exposures – 900°C

Time vs. Mass Change / Area for Crofer, E-brite, and AL453 Samples (900°C, Dry Air)

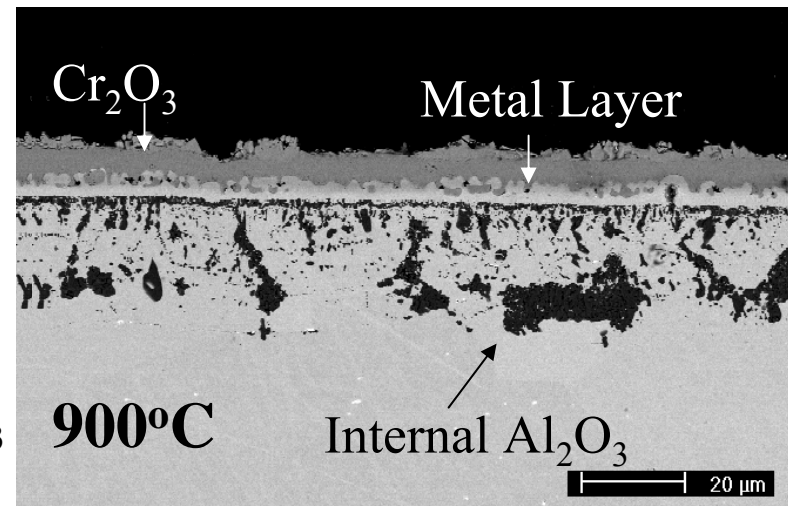
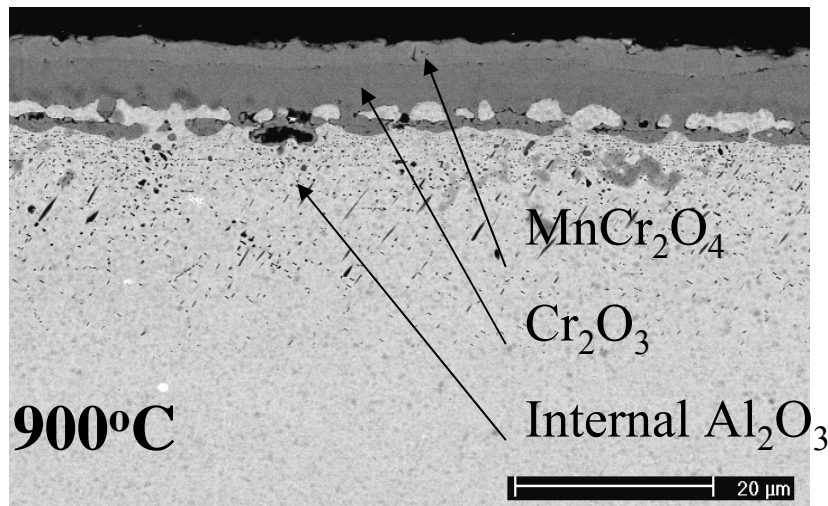
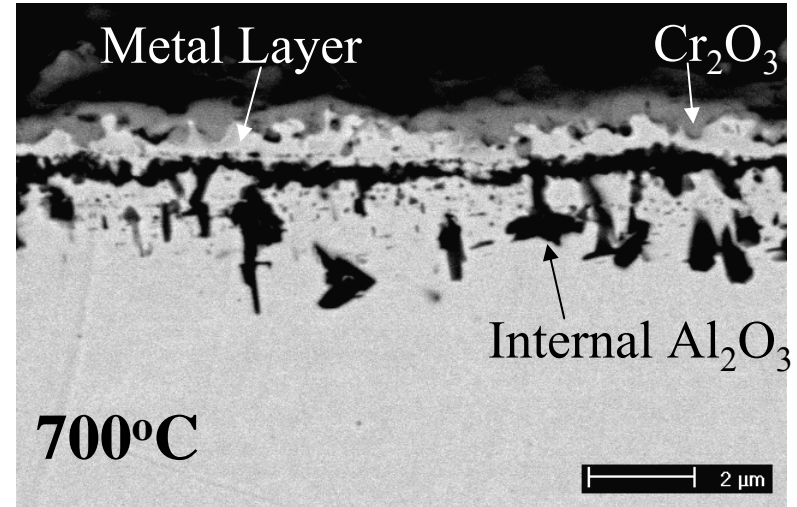


# Internal Oxidation of Impurities

## Crofer

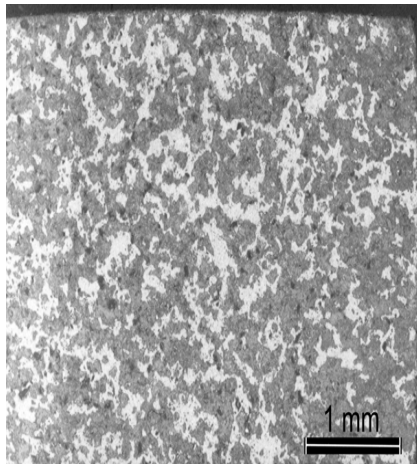


## AL453



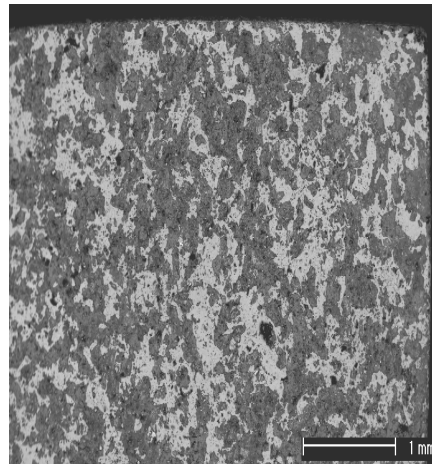
# Cyclic Oxidation of Alloys

1 h  
Cycles  
1100°C



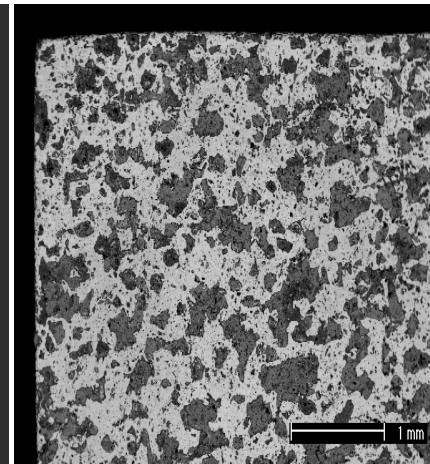
N5

dry  
615cycles



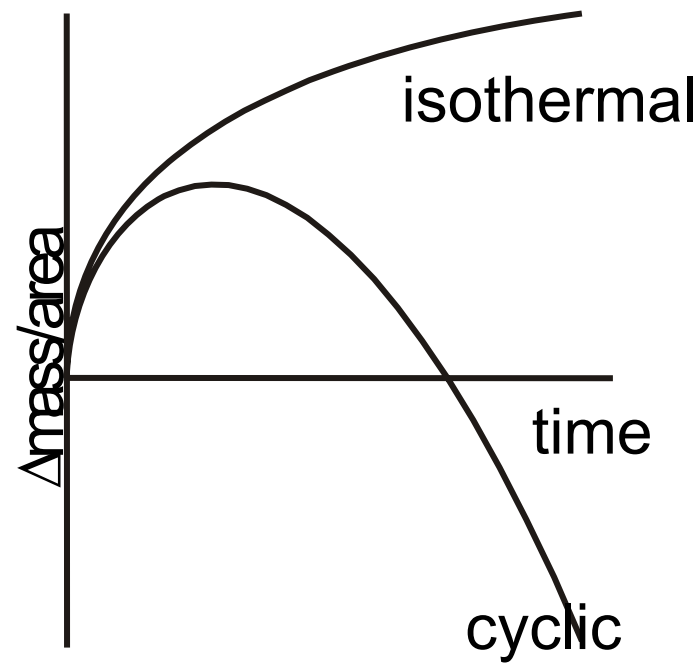
0.1atm

664cycles

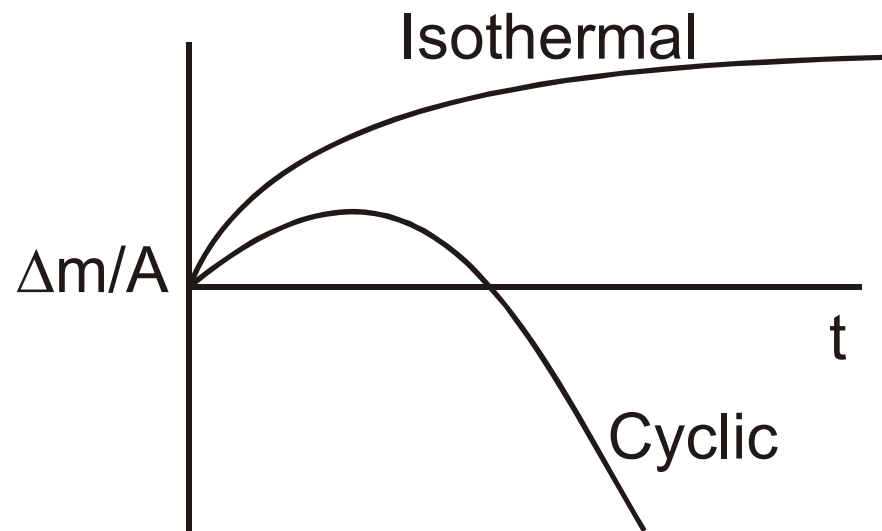
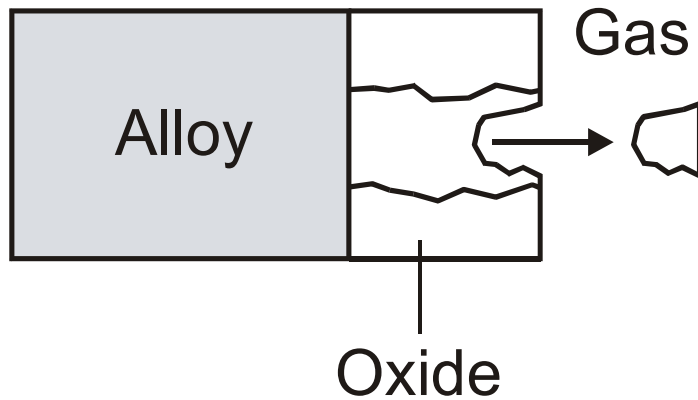


0.5atm

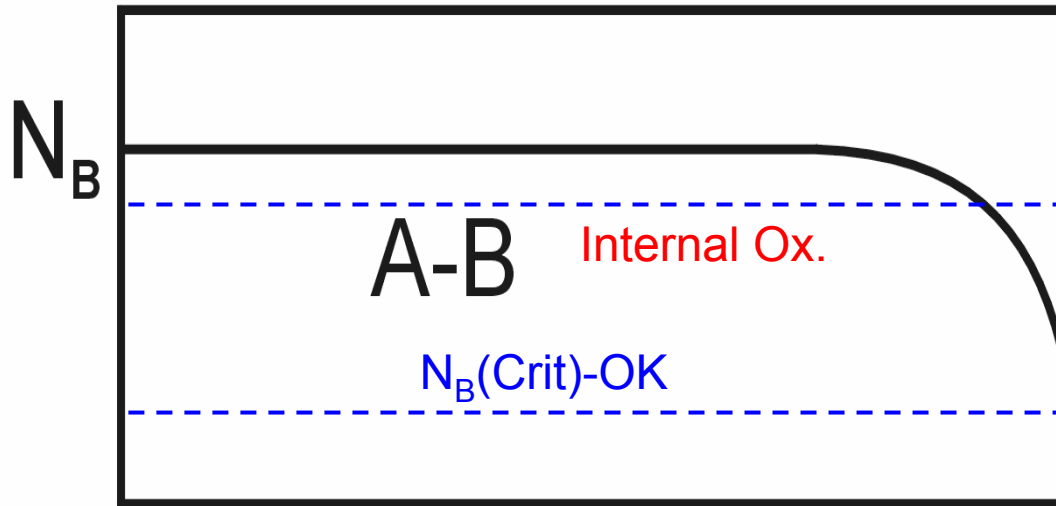
802cycles



# Cyclic Oxidation



# Effects of Alloy Depletion and Scale Spallation

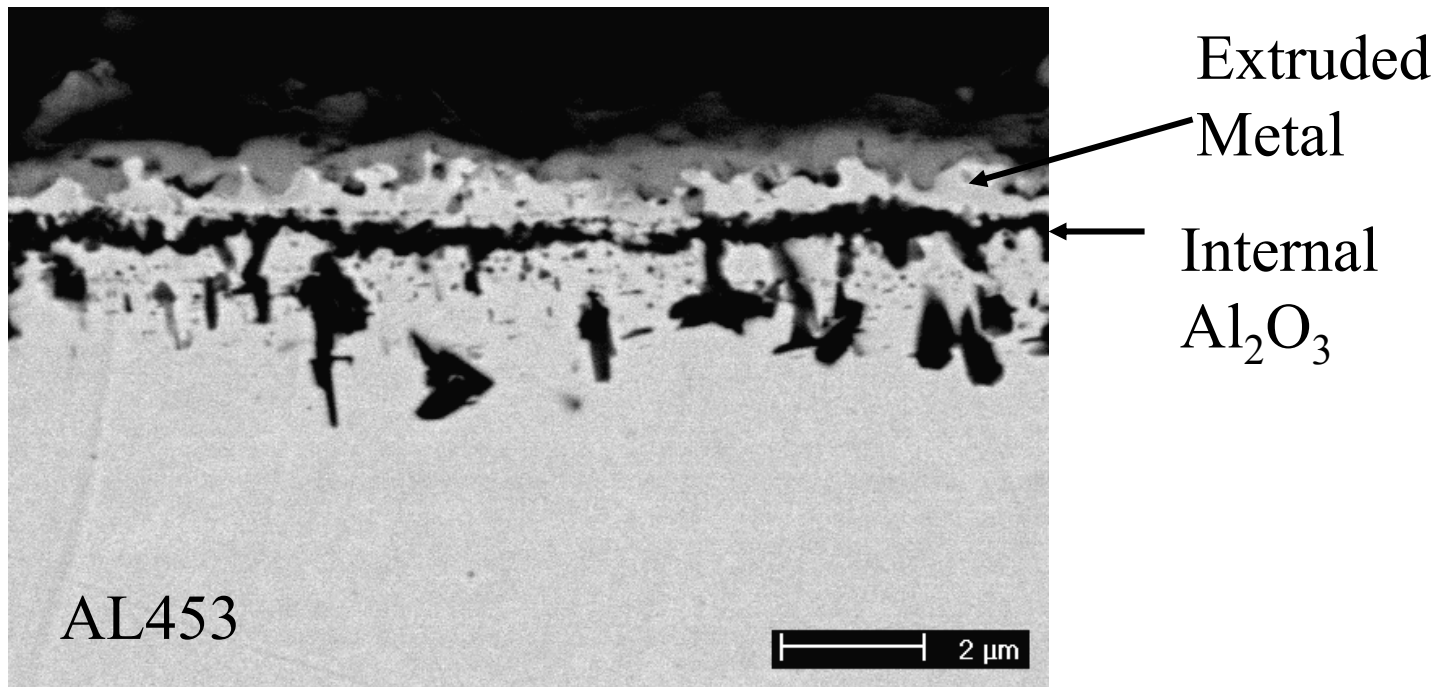


# Origins of Oxide Stress

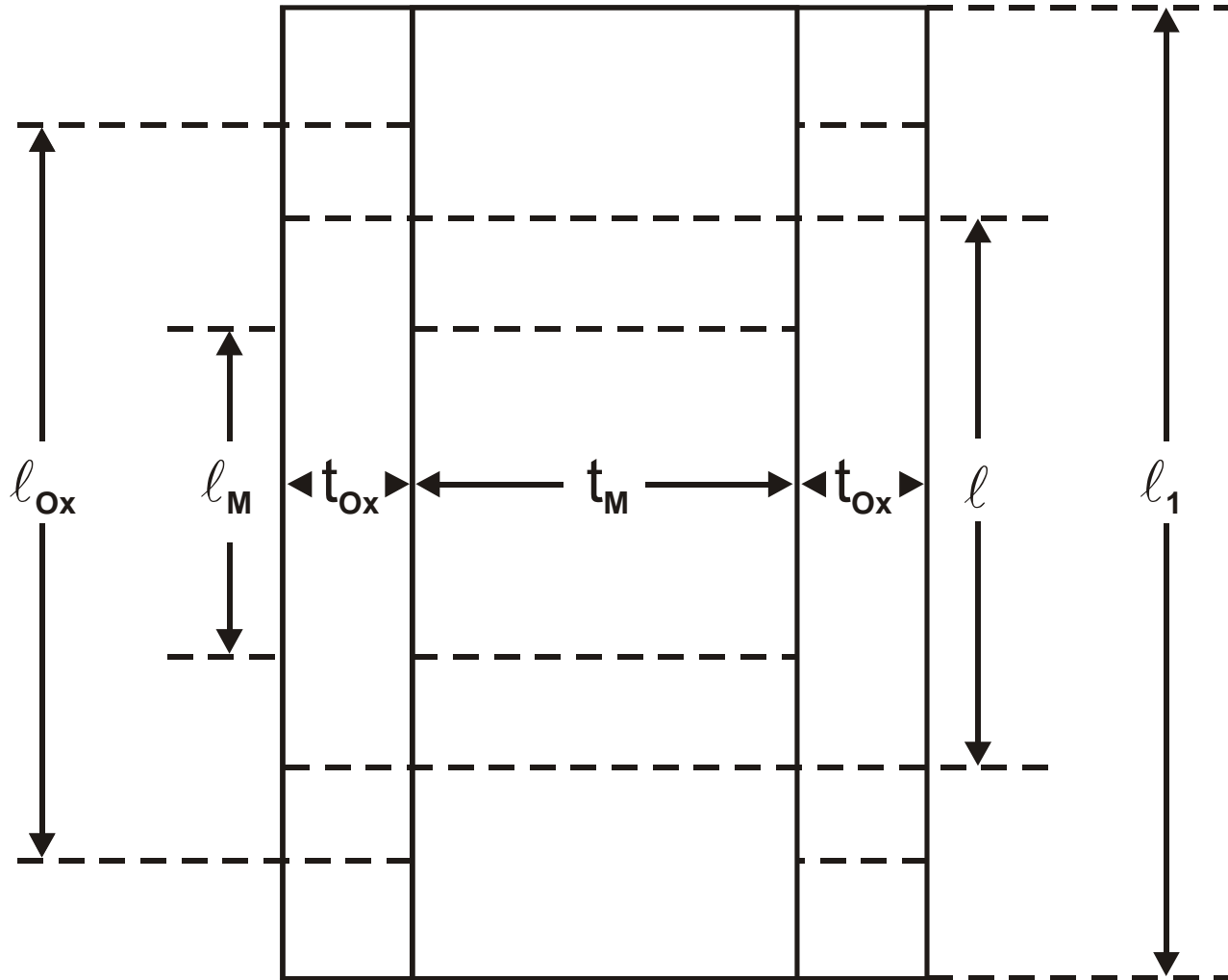
- Growth Stresses – stresses arising from the nature of the oxide growth process
- Thermal Stresses – stresses arising from the thermal expansion mismatch between metal and oxide.
- Applied Loads



# Stress Generation by Internal Oxidation



# Thermal Stress





# Origin of Thermal Stress

$$\varepsilon_{thermal}^{metal} = \alpha_M \Delta T$$

$$\varepsilon_{thermal}^{Ox} = \alpha_{Ox} \Delta T$$

$$\Delta T = T_L - T_H$$

$$\varepsilon_{mech}^{metal} = \frac{\sigma_M (1 - \nu_M)}{E_M}$$

$$\varepsilon_{mech}^{Ox} = \frac{\sigma_{Ox} (1 - \nu_{Ox})}{E_{Ox}}$$

$$\varepsilon_{thermal}^{metal} + \varepsilon_{mechanical}^{metal} = \varepsilon_{thermal}^{Ox} + \varepsilon_{mechanical}^{Ox}$$

$$\sigma_M t_M + 2\sigma_{Ox} t_{Ox} = 0 \quad \text{Force Balance}$$

$$\alpha_M \Delta T - \frac{2\sigma_{Ox} t_{Ox} (1 - \nu_M)}{t_M E_M} = \alpha_{Ox} \Delta T + \frac{\sigma_{Ox} (1 - \nu_{Ox})}{E_{Ox}}$$

$$\sigma_{Ox} = \frac{-(\alpha_{Ox} - \alpha_M) \Delta T}{\frac{2t_{Ox}(1 - \nu_M)}{t_M E_M} + \frac{(1 - \nu_{Ox})}{E_{Ox}}}$$

$$\sigma_{Ox} = \frac{-E_{Ox}(\alpha_{Ox} - \alpha_M) \Delta T}{(1 - \nu) \left( 1 + 2 \frac{t_{Ox} E_{Ox}}{t_M E_M} \right)}$$

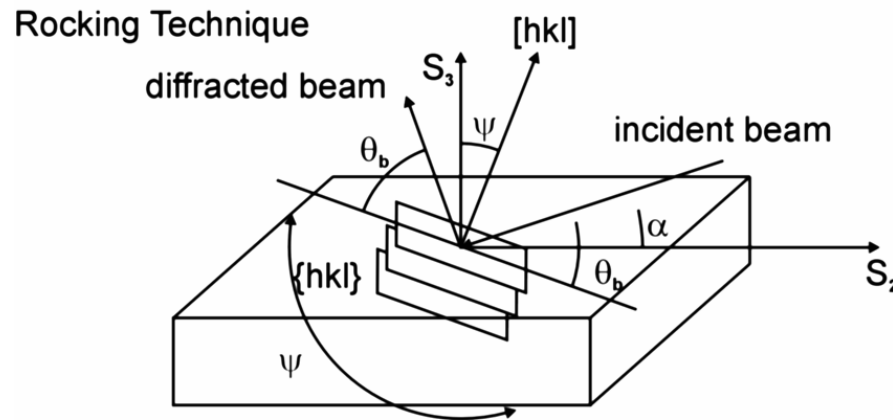
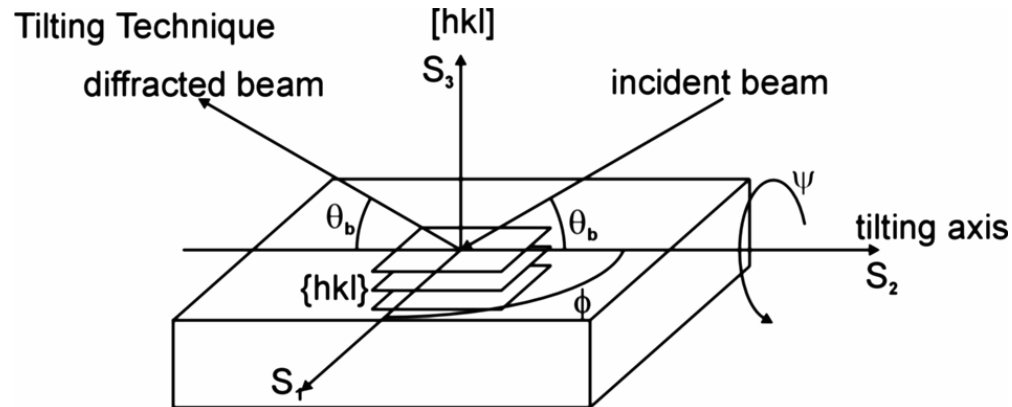
$$\text{If } \nu_M \approx \nu_{Ox}$$

Thermal Stress if  $t_{Ox} \ll t_M$

$$\sigma_{Ox} = \frac{-E_{Ox}(\alpha_{Ox} - \alpha_M)\Delta T}{(1 - \nu)}$$

# Stress Measurement

## XRD Techniques



# Stress Measurement

- d-spacing as a function of the biaxial stress and the tilt angle

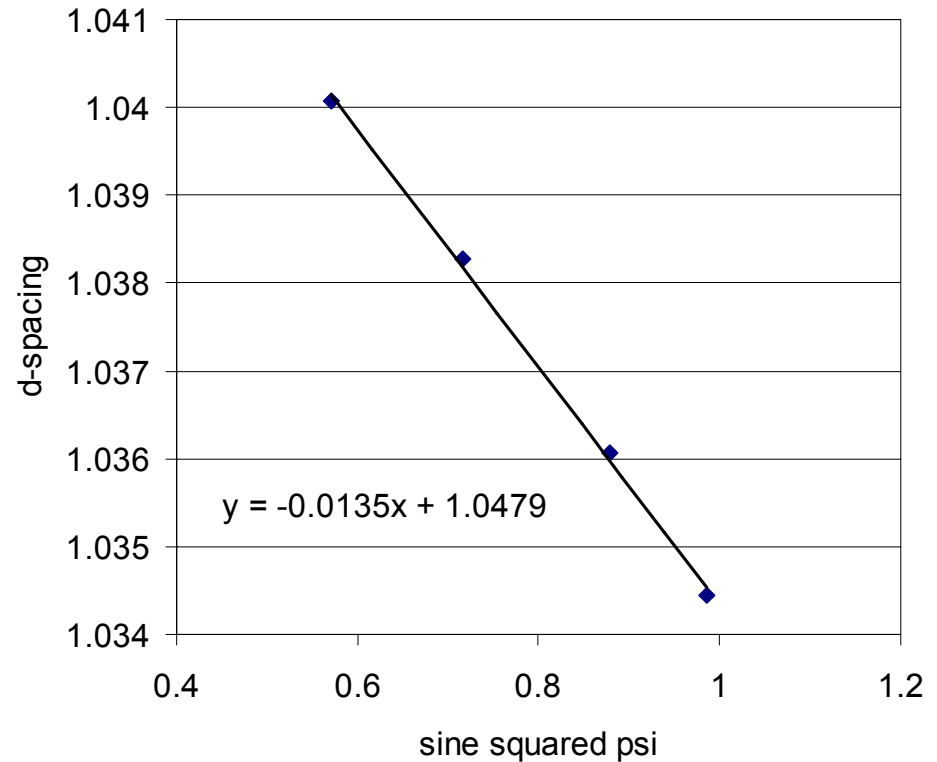
$$d_{\psi} = \frac{1}{2} s_2 \cdot \sigma_o \cdot d_o \cdot \sin^2 \psi + d_o (2s_1 \cdot \sigma_o + 1)$$

- Calculation of Stress

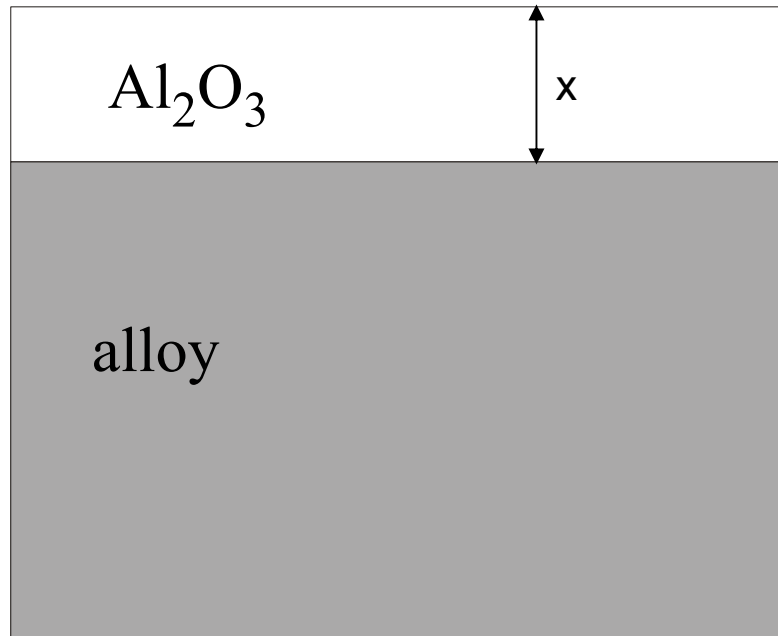
$$\text{slope} = \frac{1}{2} s_2 \cdot \sigma_o \cdot d_o$$

- 4.14 +/- 0.21 GPa

226 FIT, (Ni,Pt) aluminide, ridges removed, 40h @ 1100°C



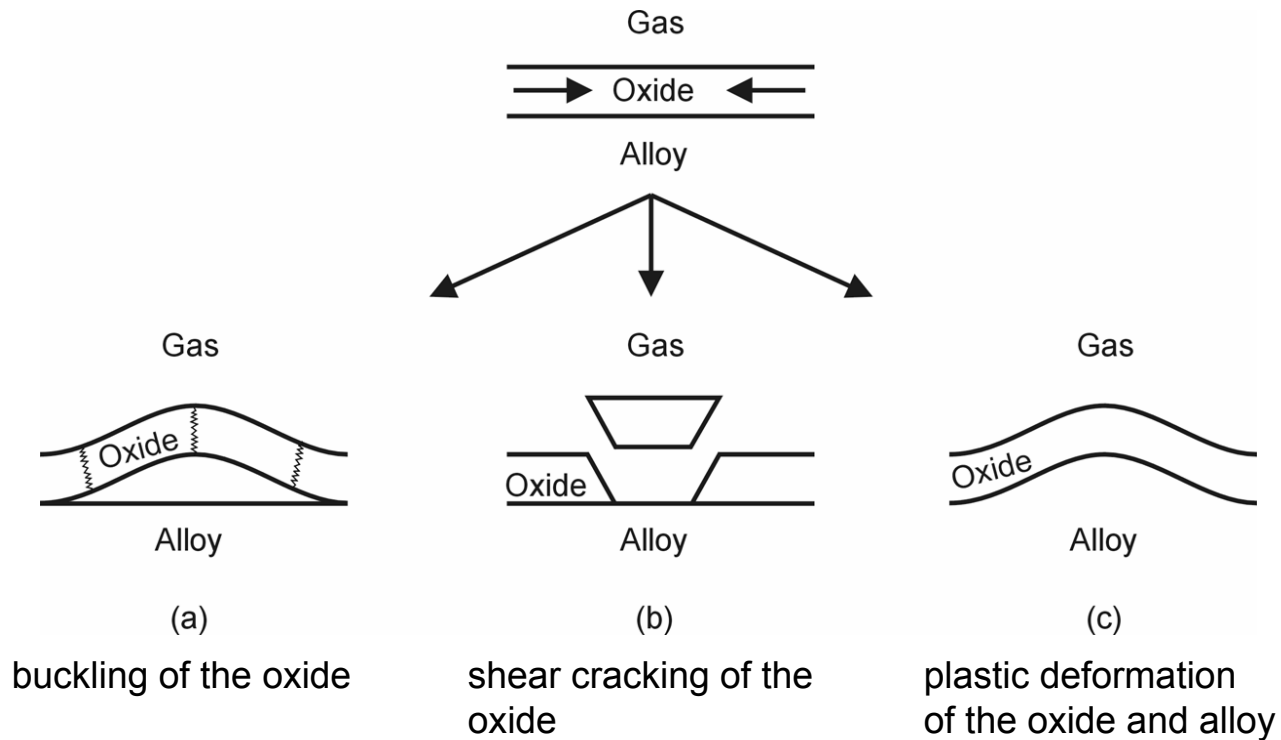
# Oxide Failure



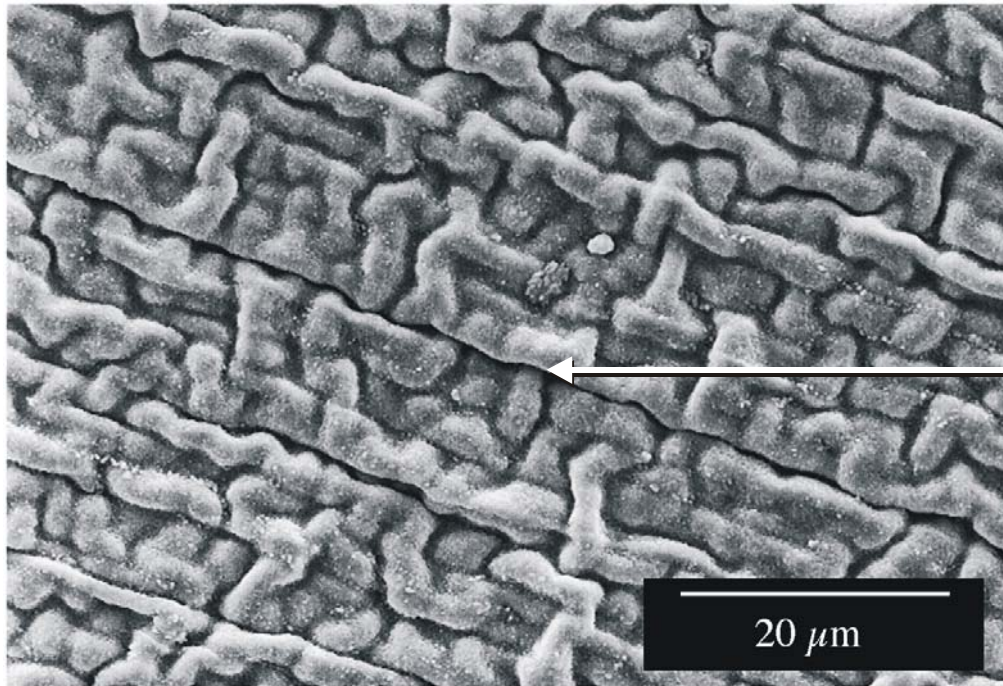
Stored elastic energy of alumina  $\approx f(s_{\text{OX}}, x_{\text{OX}})$

Fracture resistance of the alumina/alloy interface  $\approx f(\text{morphology, composition})$

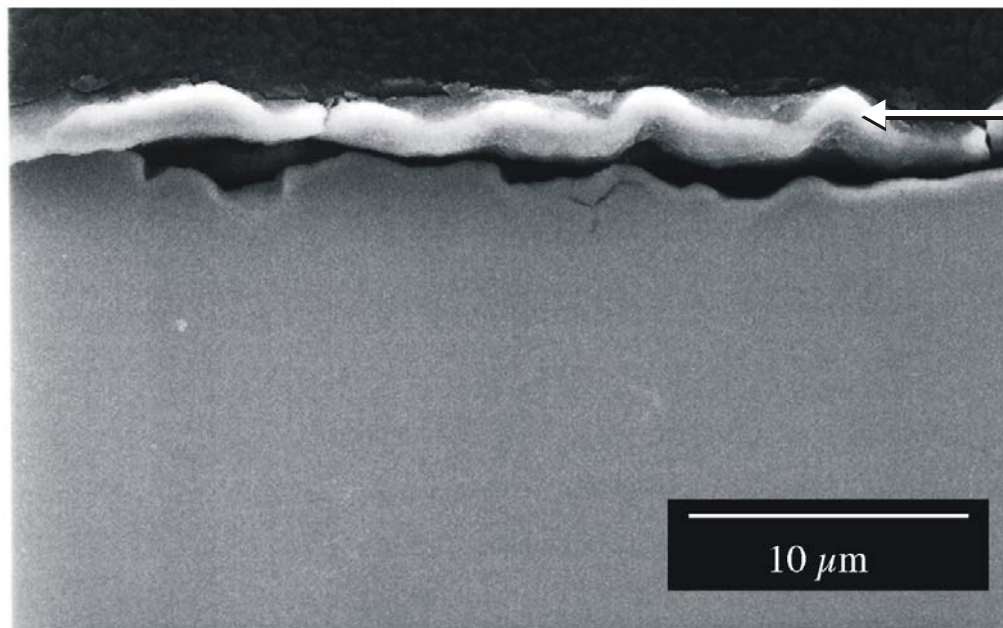
# Response to Stresses



## Example of Buckling



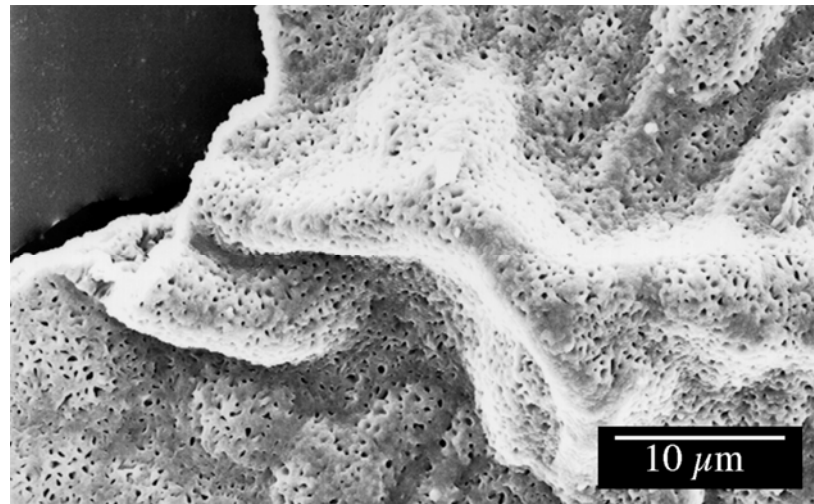
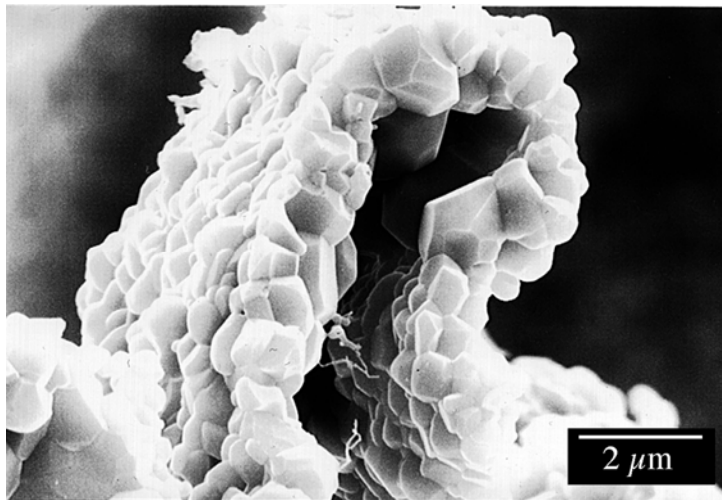
Polishing  
mark



Alumina  
scale

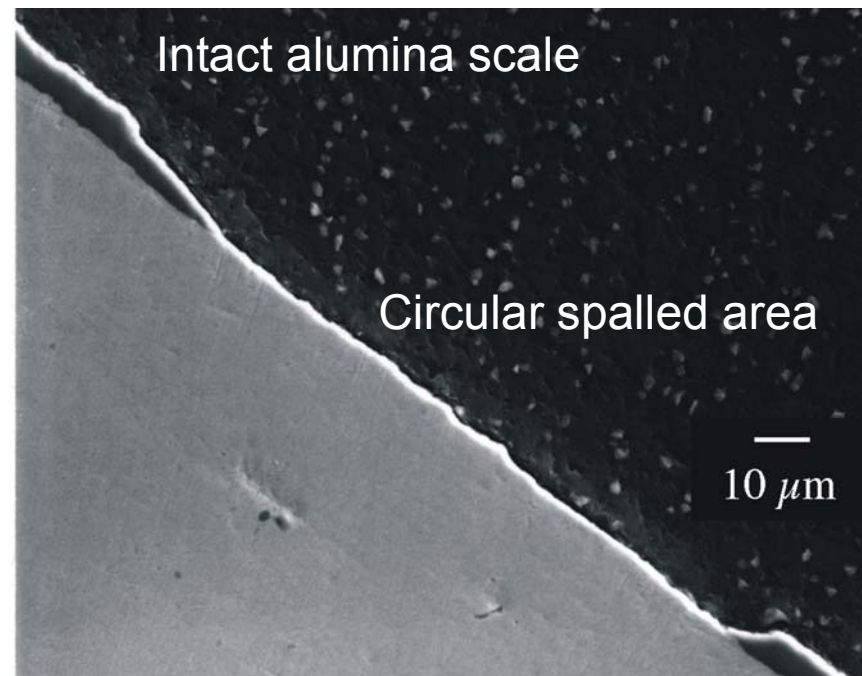
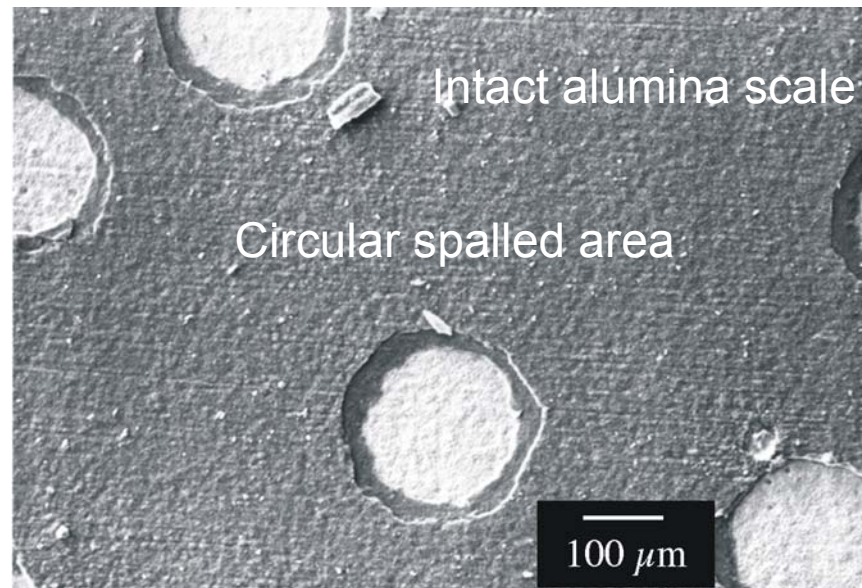
# Spallation of Alumina Scale by Buckling

FeCrAl (TMP) oxidized at 1100°C for 120 hours.

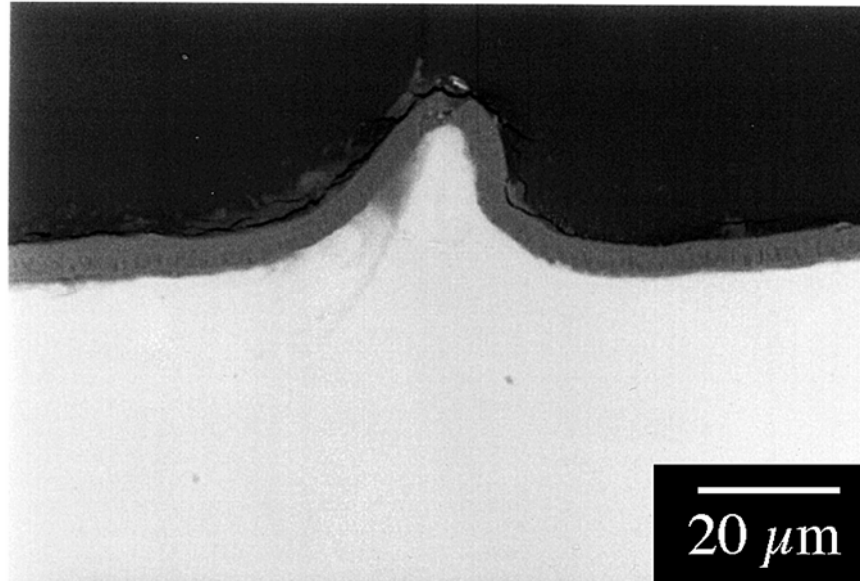




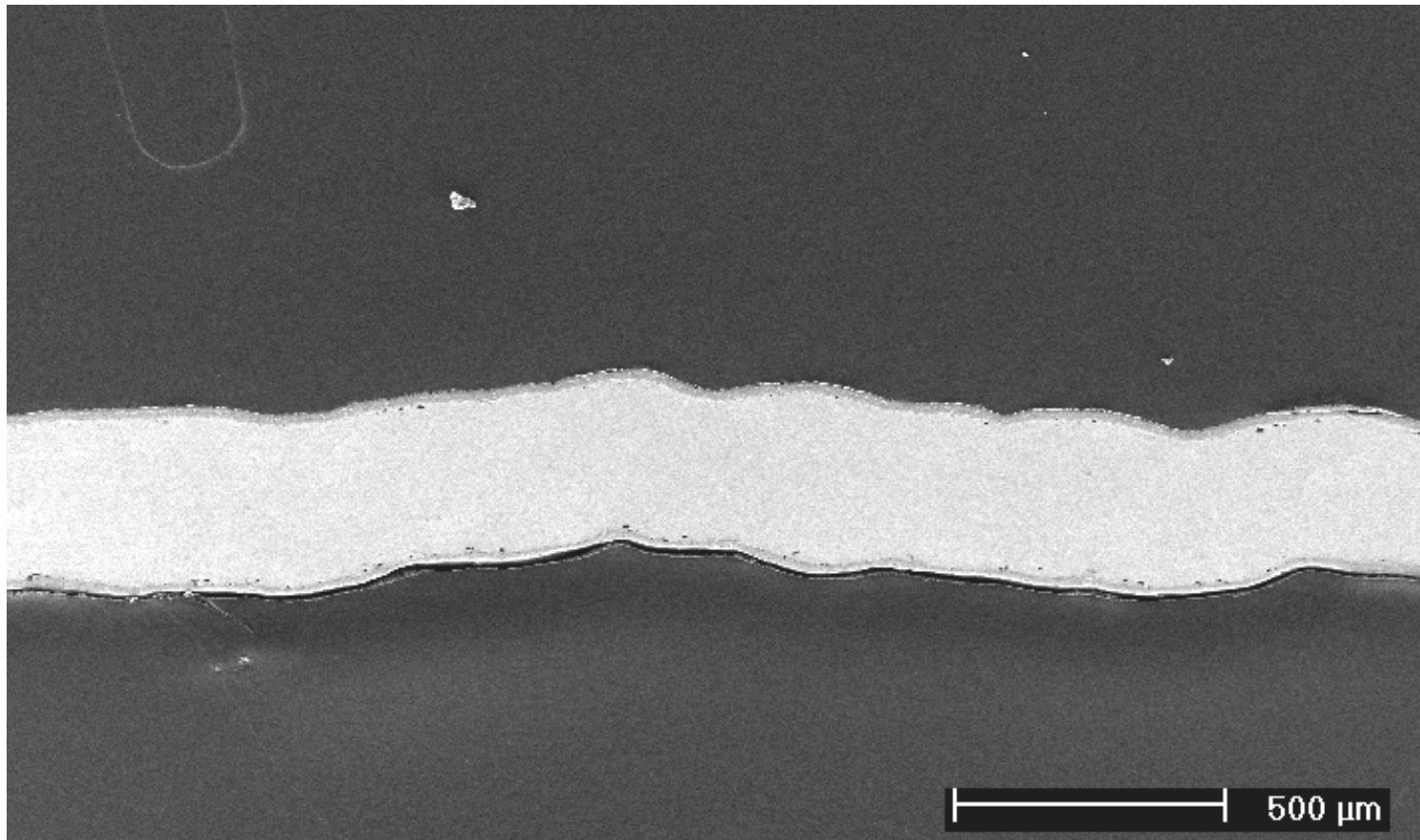
# Circular Buckles



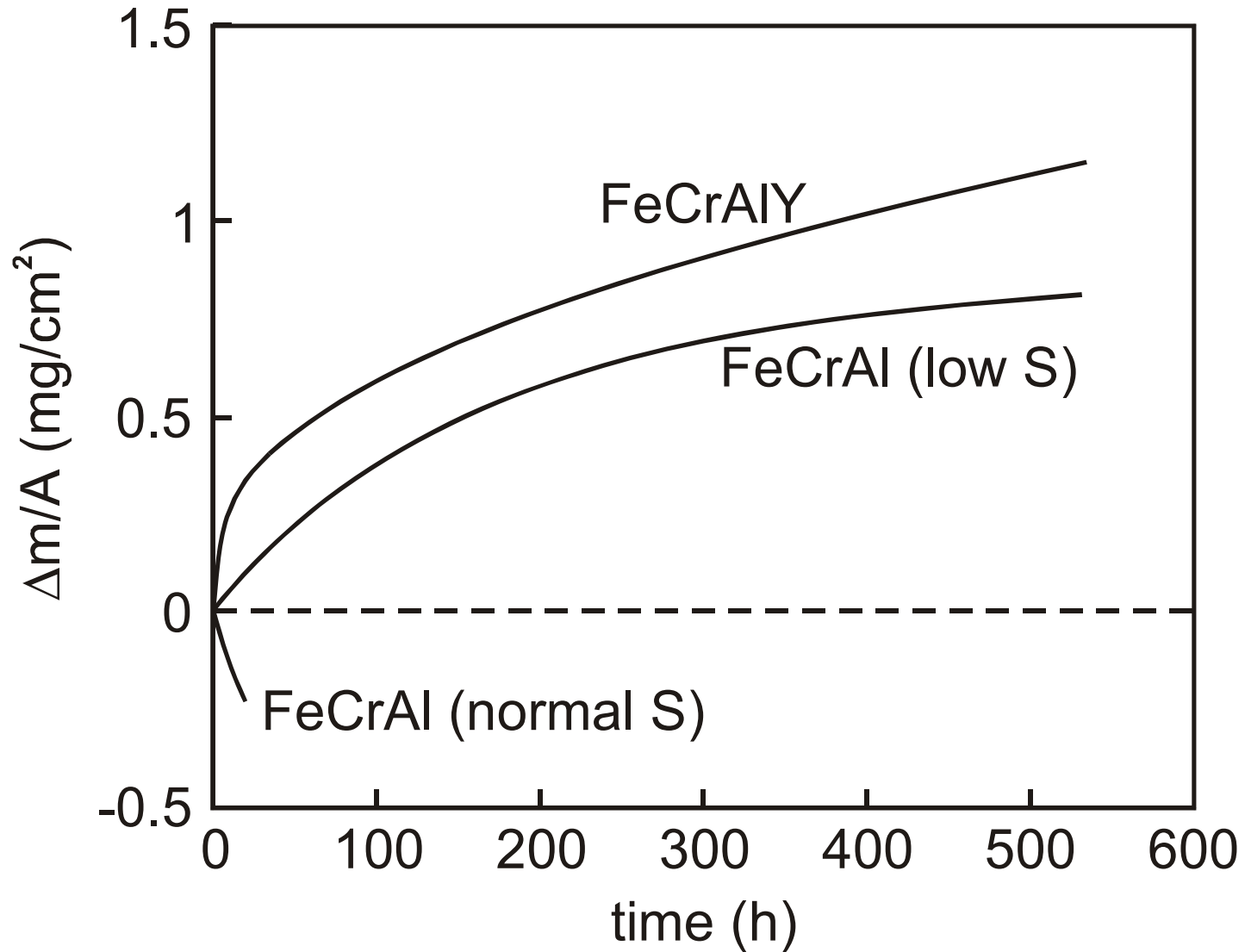
# FeCrAlTi Cyclically Oxidized for 288h at 1100°C



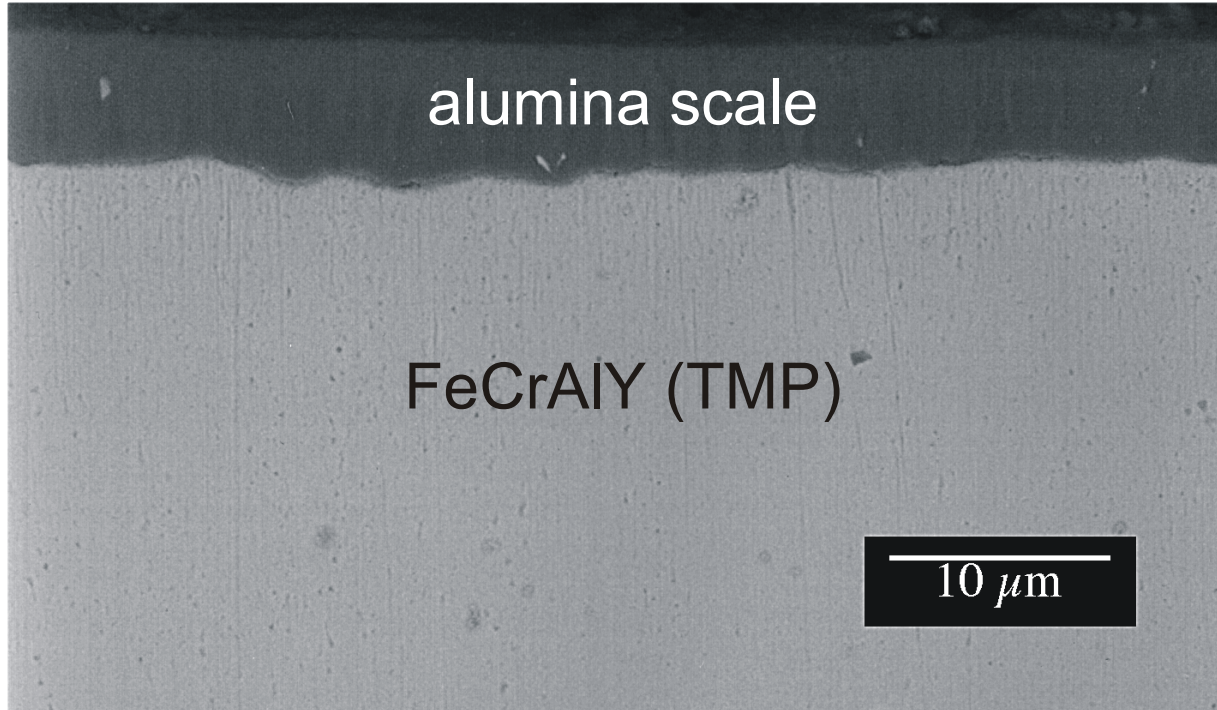
# Deformation of Crofer During Cyclic Oxidation



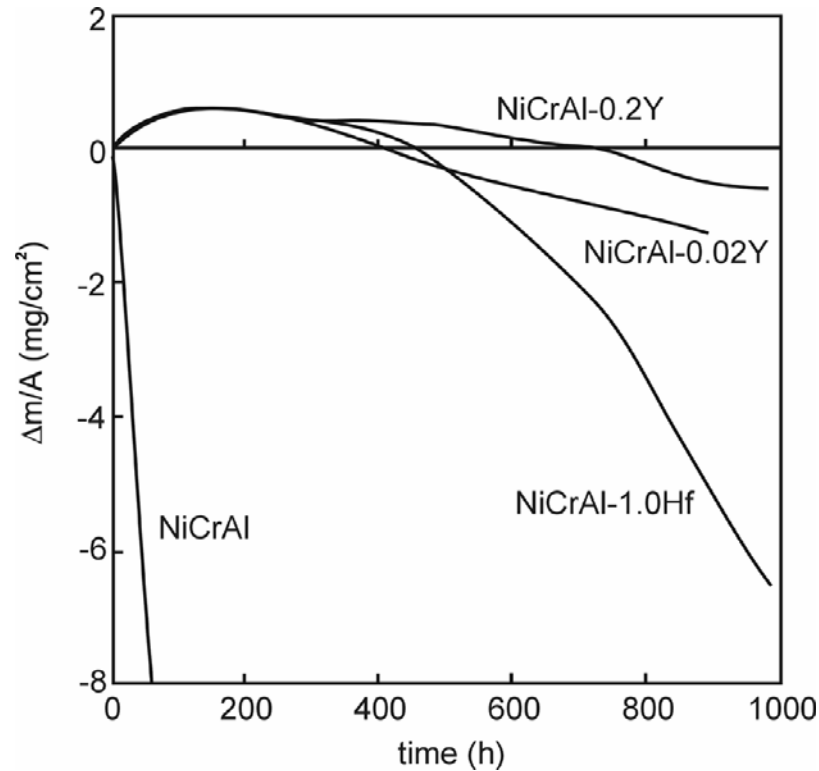
# Effect of Sulfur and Reactive Element



# Effect of Yttrium



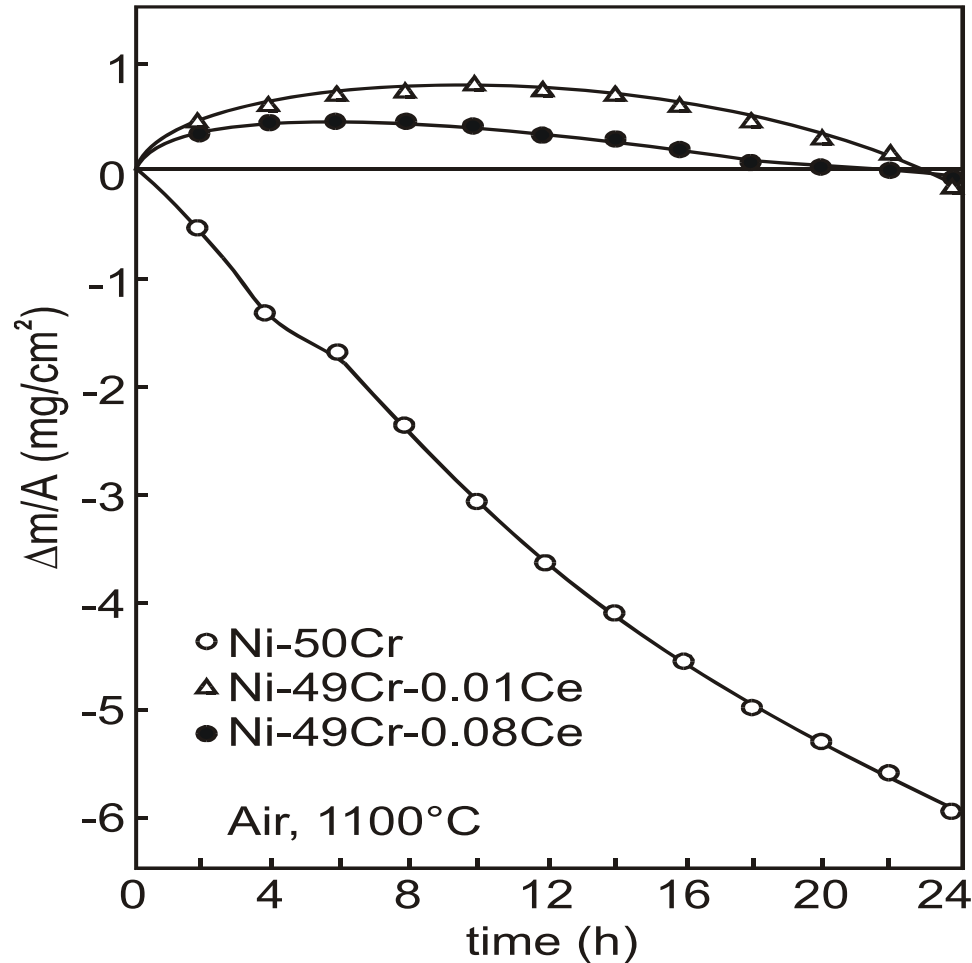
# Long Term Cyclic Oxidation Testing



Cyclic oxidation kinetics for several Ni-Cr-Al alloys exposed at 1100°C.



# Reactive Element Effect for a Chromia Former

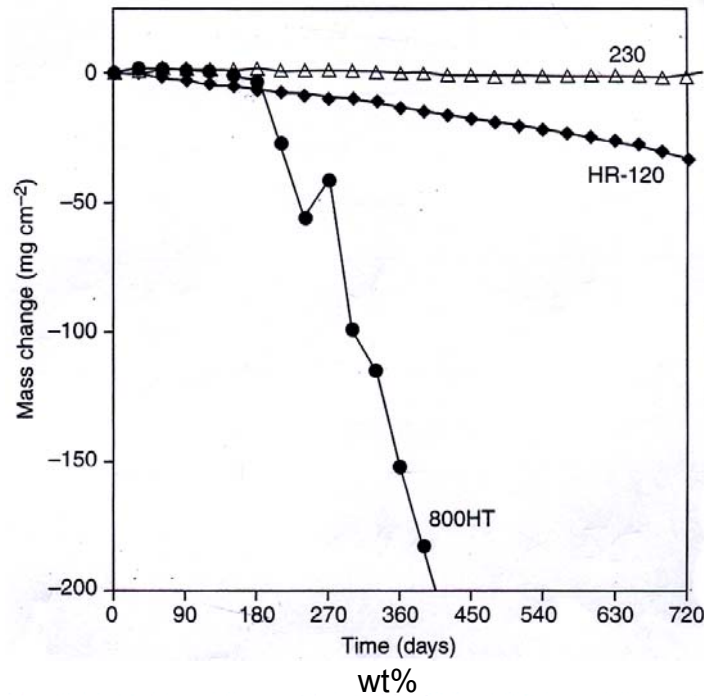


Cyclic  
Oxidation

# Cyclic Oxidation Degradation and Breakaway

- Alloys initially are  $\text{Cr}_2\text{O}_3$ -formers

982°C 30 day cycles



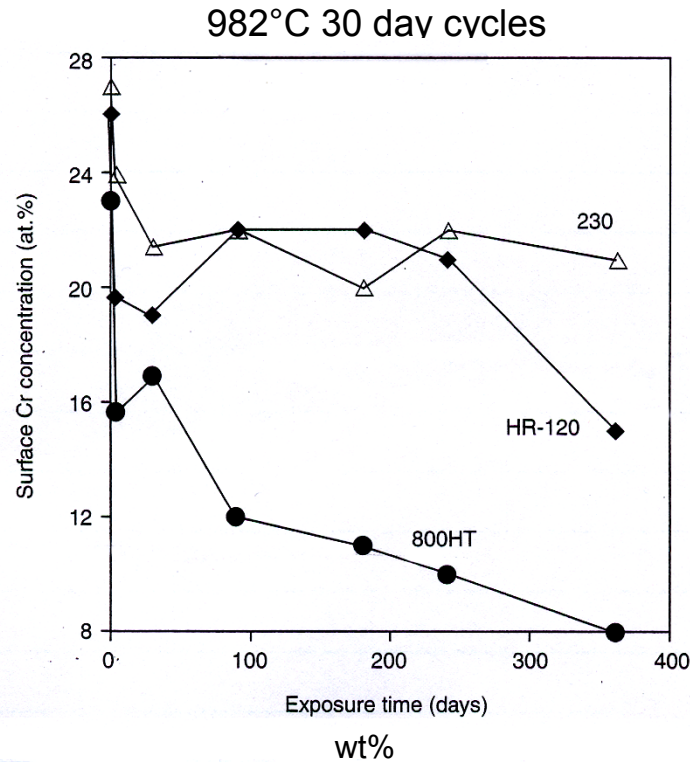
Alloy	Cr	Ni	Fe	Co	Mo	W	C	Others
800HT	21	32.5	Bal.	—	—	—	0.08	0.8Mn, 0.5Si, 0.4Cu, 0.4Al, 0.4Ti
HR-120	25	37	Bal.	3*	2.5*	2.5*	0.05	0.7Mn, 0.7Nb, 0.6Si, 0.2N, 0.1Al, 0.005B
230	22	Bal.	3*	—	2	14	0.1	0.5Mn, 0.4Si, 0.3Al, 0.02La, 0.015B*

More adherent oxide



# Cyclic Oxidation Degradation and Breakaway

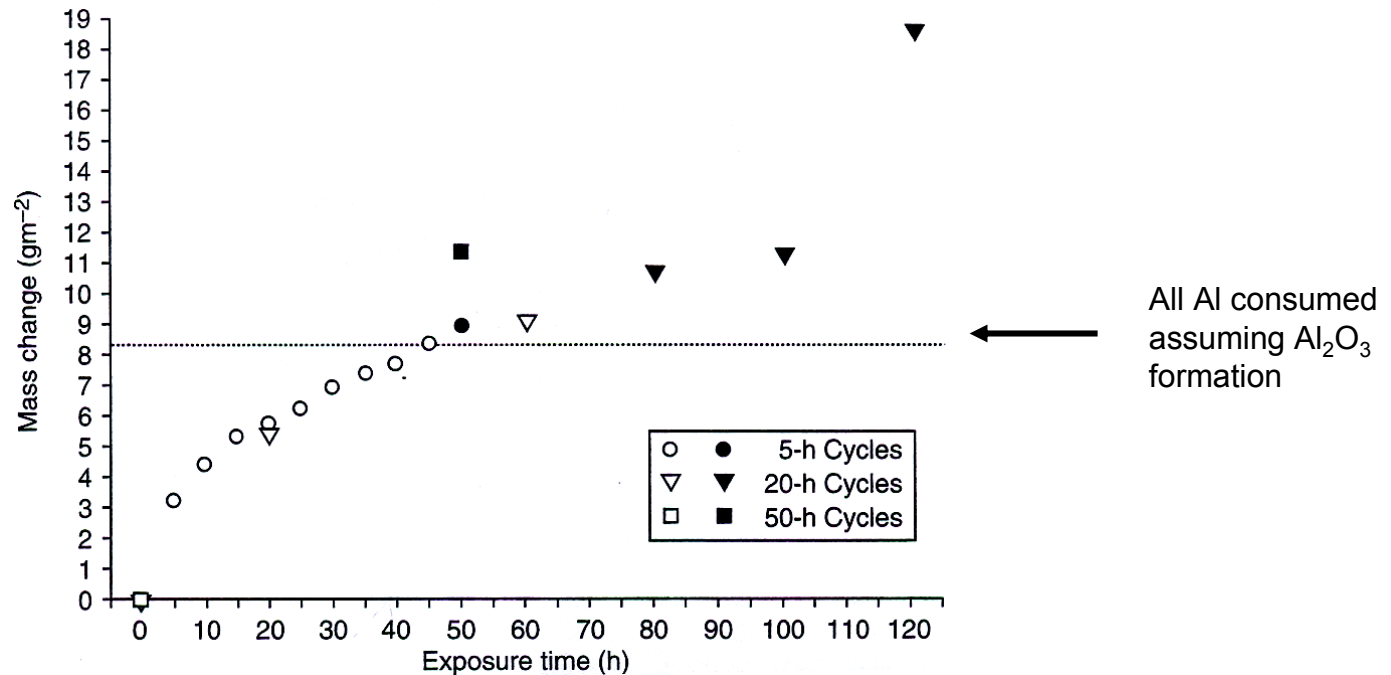
- Chromium depletion due to spalling of oxide



Alloy	Cr	Ni	Fe	Co	Mo	W	C	Others
800HT	21	32.5	Bal.	—	—	—	0.08	0.8Mn, 0.5Si, 0.4Cu, 0.4Al, 0.4Ti
HR-120	25	37	Bal.	3*	2.5*	2.5*	0.05	0.7Mn, 0.7Nb, 0.6Si, 0.2N, 0.1Al, 0.005B
230	22	Bal.	3*	—	2	14	0.1	0.5Mn, 0.4Si, 0.3Al, 0.02La, 0.015B*

# Cyclic Oxidation Degradation and Breakaway

- Alloy initially is an  $\text{Al}_2\text{O}_3$ -Former

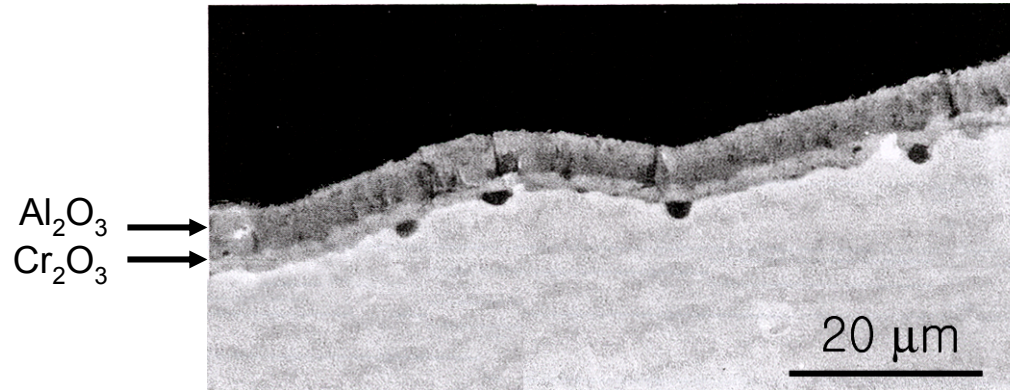


(wt%) Fe-20.5Cr-5.2Al-0.002Zr-0.39Si-0.01Ti-0.25Mn  
1200°C

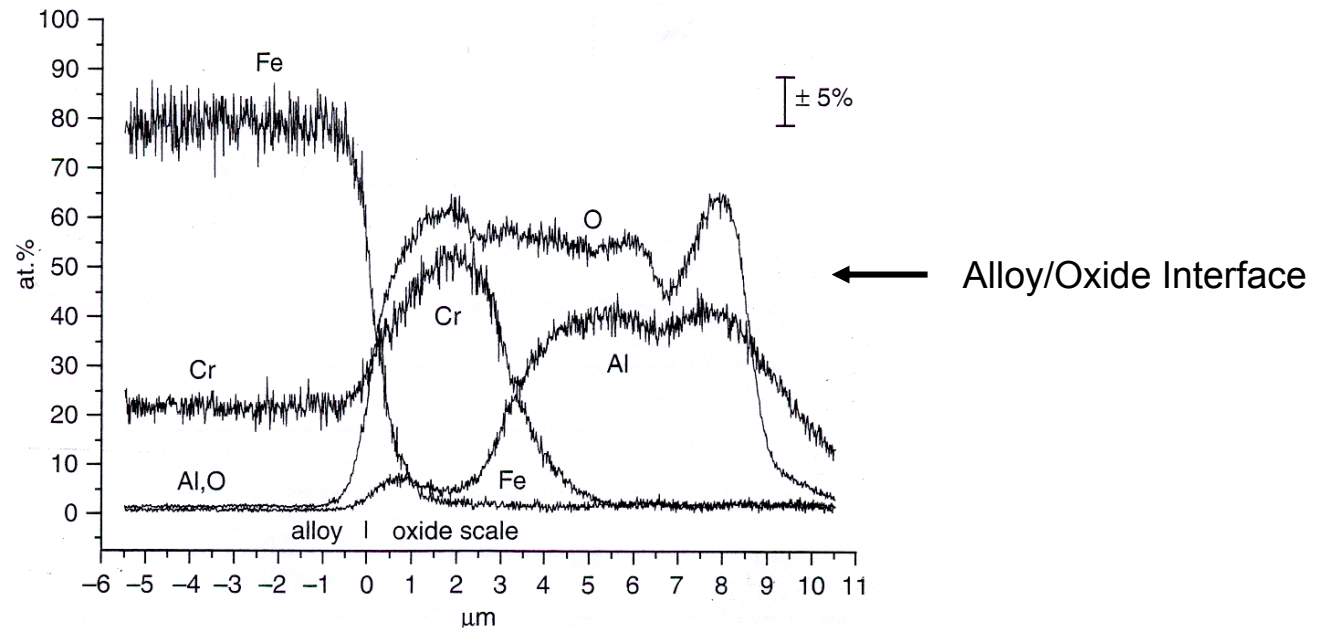
Filled Symbols First Evidence of Color Change

# Cyclic Oxidation Degradation and Breakaway

- Fe-20.3Cr-5.6Al-0.05Y-0.04Zr-0.26Si-0.2Mn

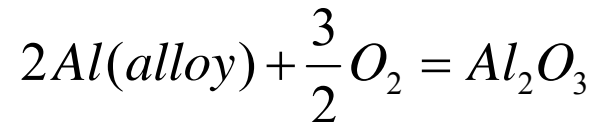


1200°C, 160 hr  
20 hr cycles  
air



# Oxidation of Al and Cr In a Fe-25Cr-5Al(wt%) Alloy

- At 1200°C to oxidize aluminum:



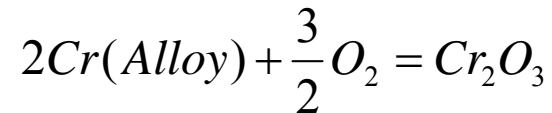
$$\Delta G_{Al_2O_3}^{\circ} = -288,091 \frac{cal}{mole}$$

$$K = e^{-\frac{\Delta G_{Al_2O_3}^{\circ}}{RT}} = \frac{1}{a_{Al}^2 P_{O_2}^{3/2}}$$

$$\frac{\frac{Gas}{Al_2O_3}}{\frac{Alloy}}{\leftarrow} P_{O_2} = \frac{2.43 \times 10^{-29}}{a_{Al}^{4/3}}$$

# Oxidation of Al and Cr In a Fe-25Cr-5Al(wt%) Alloy

- Similarly the oxygen pressure to oxidize chromium in the alloy is



$$\Delta G_{Cr_2O_3}^{\circ} = -180,740 \frac{cal}{mole}$$

$$P_{O_2} = \frac{1.12 \times 10^{-18}}{a_{Cr}^{4/3}}$$

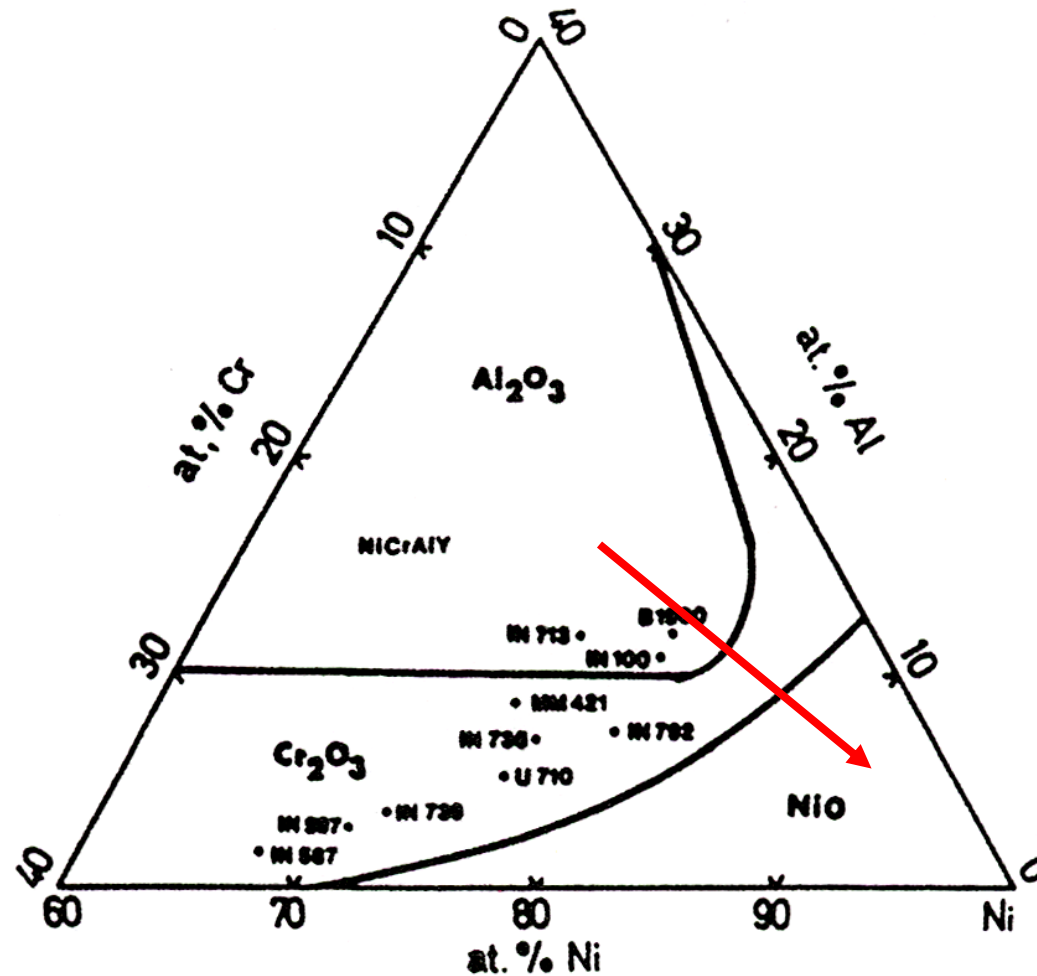
$$\text{if } a_{Al} \sim 10^{-2} \quad (P_{O_2})_{Al_2O_3/Alloy} = 1.1 \times 10^{-26} atm$$

$$a_{Cr} \sim 0.25 \quad (P_{O_2})_{oxidizeCr \text{ in } Alloy} = 7.1 \times 10^{-18} atm$$

Chromium will not be oxidized until  $P_{O_2} = 1.8 \times 10^{-17}$  hence  $a_{Al}$  must be reduced to:

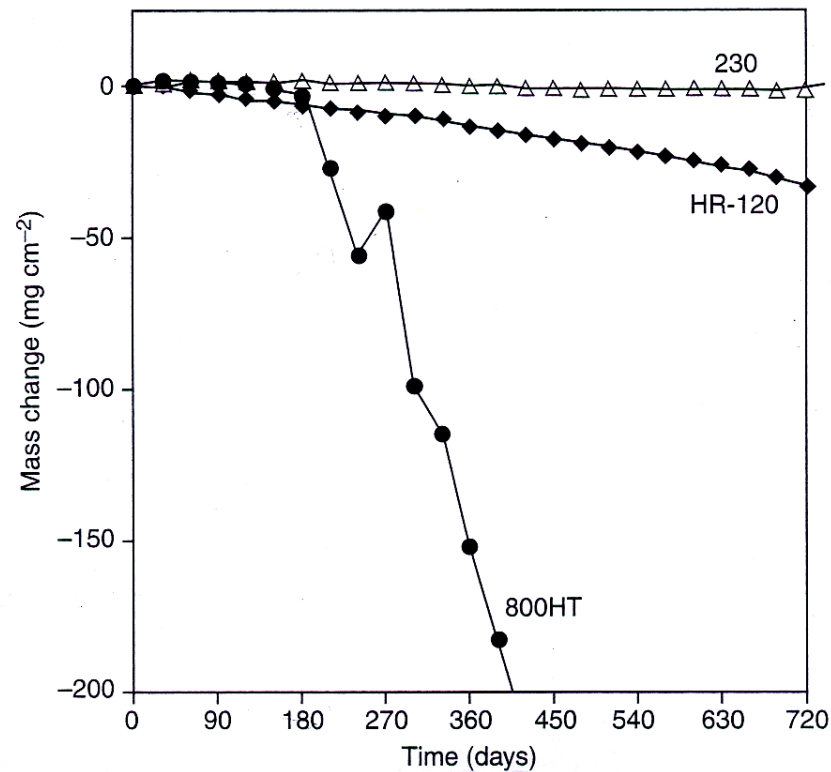
$$a_{Al} = 2.5 \times 10^{-9} atm$$

# Ni-Cr-Al Cyclic Oxidation Degradation



# Cyclic Oxidation Degradation versus Breakaway

- The difference between cyclic oxidation degradation and breakaway is somewhat subtle:

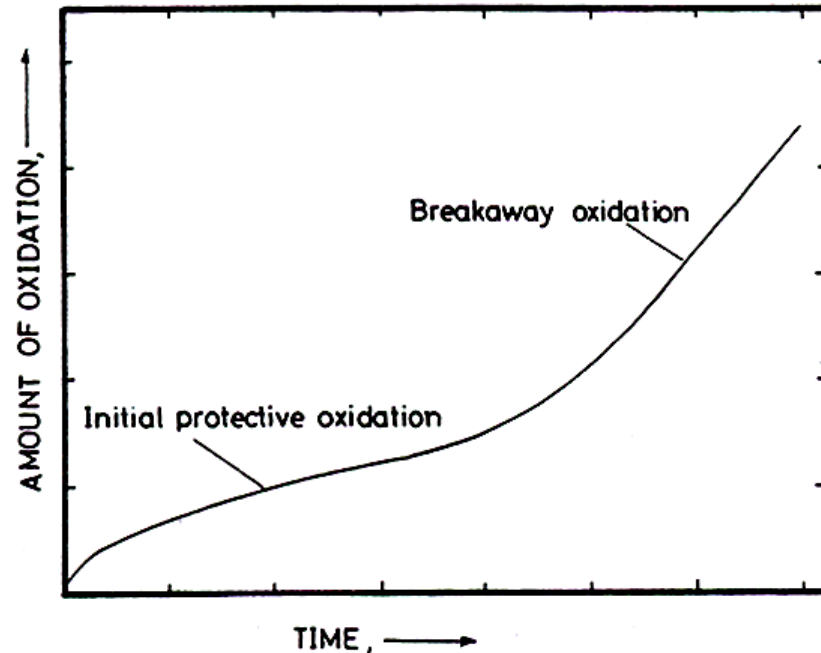


Cyclic oxidation degradation

Breakaway

Cyclic Oxidation at 982°C

# Breakaway Can Also Occur Under Isothermal Conditions



Schematic illustration of the kinetics of breakaway oxidation.

- When breakaway is observed under isothermal conditions, the alloy usually is not very oxidation resistant (e.g. Zr, Nb)
- If the alloy is oxidation resistant extremely long isothermal oxidation exposures are required at high temperatures.

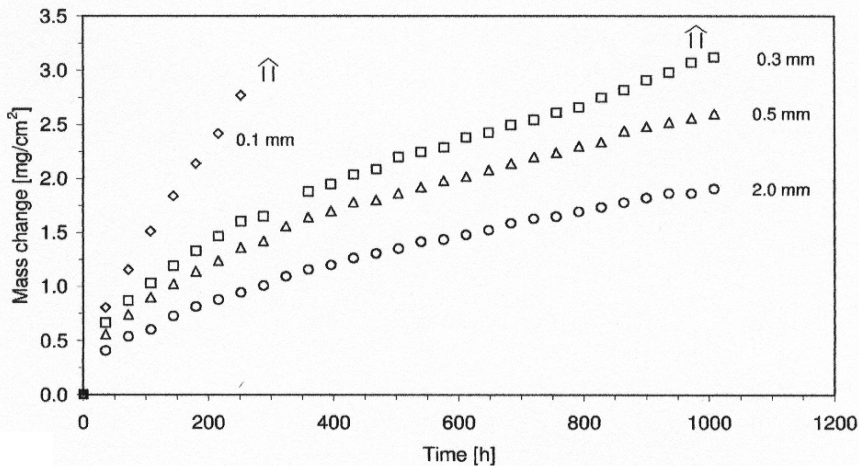


# Lifetime Prediction to Breakaway

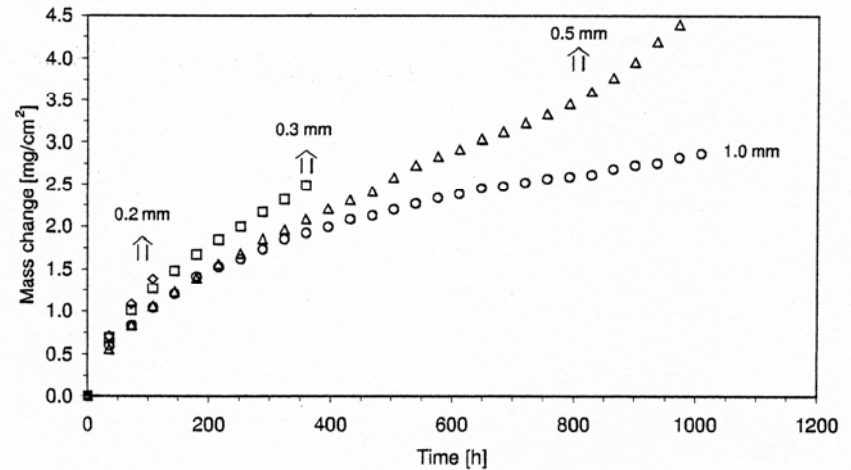
900°C

## Lifetime Prediction

Crofer 22APO



ZMG 232

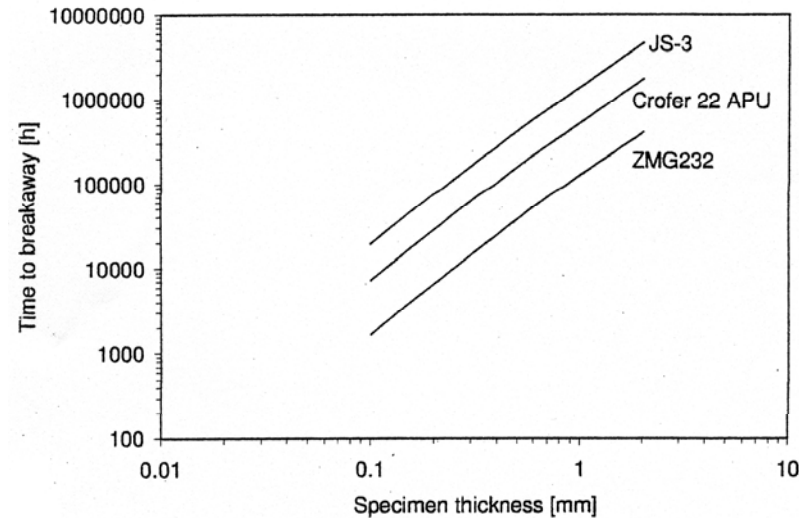


Cyclic Oxidation (2 hr hot, 15 min cool)

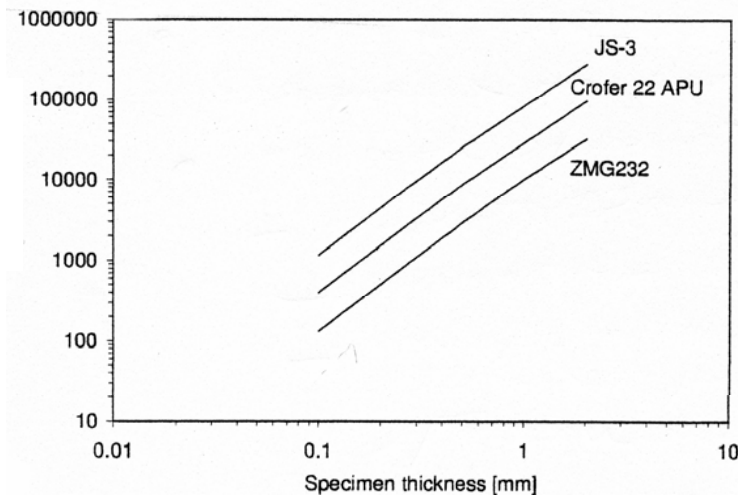
Composition (wt%)

Steel	Fe	Cr	Mn	Ti	La	Si	Al	Ni	Zr	C	N	S
Crofer 22APU	Bal.	22.6	0.4	0.06	0.07	0.11	0.12	0.16	-	0.005	0.01	<0.001
ZMG232	Bal.	22.1	0.48	-	<0.01	0.36	0.19	0.31	0.13	0.0017	0.0047	<0.001

# Calculated Lifetime

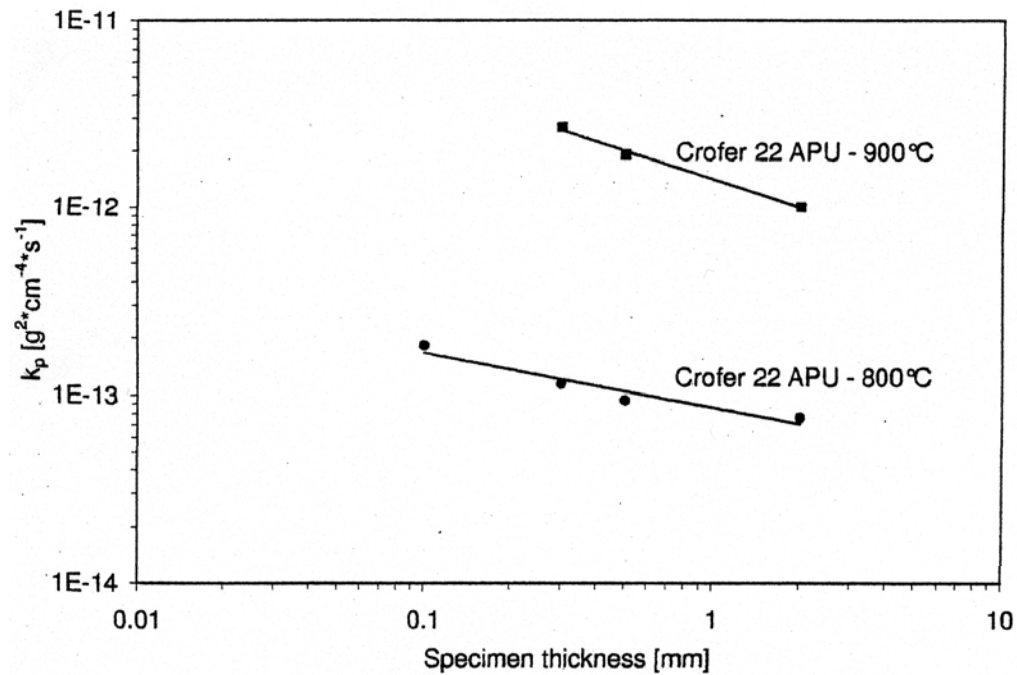


800°C



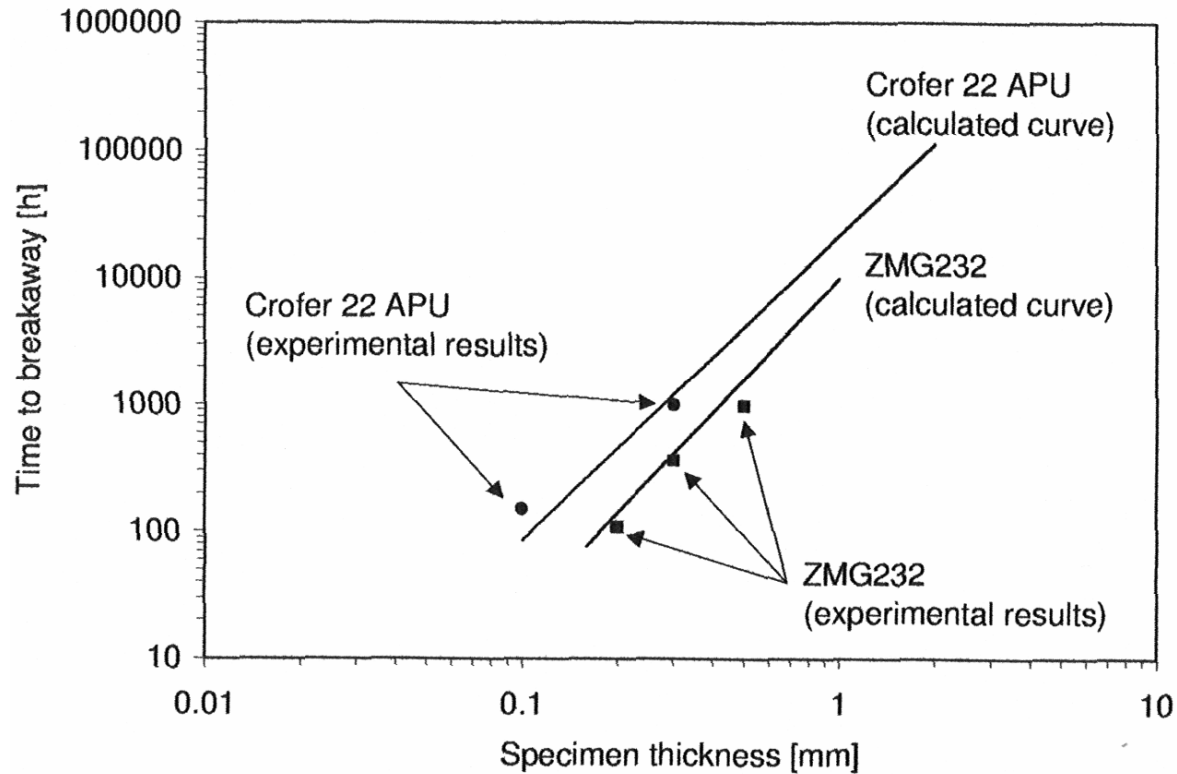
900°C

- no oxide spalling
- $k_p$  values for thick specimens
- breakaway occurs when Cr is reduced to some critical level



- Parabolic rate constants are dependent on specimen thickness
- Possible explanation:
  - Growth stresses in oxide
  - Manganese depletion
  - Minor alloying elements (Si, Ti, Al) internal oxidation with alloy extension

900°C



Correlation of calculated and experimental results considering thickness dependence of  $k_p$ .